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Laboratory Evaluation of Nonmethane Organic Carbon Determination in Ambient Air by Cryogenic Reconcentration and Flame Ionization Detection

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LABORATORY EVALUATION OF NONMETHANE ORGANIC CARBON DETERMINATION IN AMBIENT AIR BY CRYOGENIC PRECONCENTRATION AND FLAME IONIZATION DETECTION

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16. ABSTRACT

The results of this study demonstrate the feasibility of a technique for analyzing samples of ambient air for gaseous non methane organic compounds (NMOC) using a cryogenic trap to both preconcentrate and separate NMOC from methane (CH_4). The NMOC is subsequently measured by warming the trap to release the NMOC and channeling the concentrated sample of NMOC into a modified commercial flame ionization detector. The system response per carbon atom is linear and uniform for a large group of hydrocarbons analyzed singly or in mixtures. Analyses of aromatic hydrocarbons indicate a reduced per-carbon response that varies from compound to compound but is linear with concentration. Precision has been found to be within ±5 percent for standard gas calibrations and generally ±10 percent for ambient samples. Accuracy for ambient air samples has been determined to be ±15 percent by comparison with compound-specific GC analysis. Experimental results also show no significant effect from humidity over a wide range of concentrations (75 to 5,000 ppbc). The analytical method is simple, rapid, and cost effective, and the NMOC measurements can be used to establish a basis for control of hydrocarbon emissions in order to meet oxidant criteria levels.

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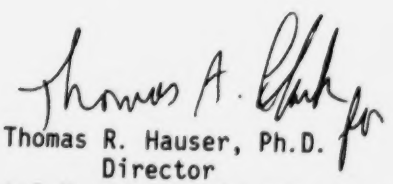
FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of Agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

As part of the assessment of environmental monitoring technology, this document summarizes an evaluation of a cryogenic trapping and concentration procedure for ambient measurements of nonmethane organic compounds (NMOC) in the atmosphere. Although NMOC monitoring is not required, per se, such data are vitally important in some areas for planning the hydrocarbon control strategy necessary to achieve the National Ambient Air Quality Standard for ozone. This evaluation of an alternative NMOC measurement technique should be beneficial to control agencies making ambient NMOC measurements for this purpose.



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ABSTRACT

This report describes the development and testing of a procedure for measurement of gaseous nonmethane organic compounds (NMOC) in ambient air. The procedure uses cryogenic trapping to preconcentrate the NMOC and separate it from methane (CH_4) and a flame ionization detector (FID) for subsequent measurement of the NMOC after it is revolatilized.

The design and the procedure for using the cryogenically cooled sample trap were critical to the successful implementation of this technique. A stainless steel tube, 0.21 cm inner diameter and 120 cm in length, efficiently trapped almost all of the hydrocarbons tested. The use of liquid argon is recommended as the cryogen, although liquid oxygen can be used if appropriate safety precautions are taken.

Cryogenic preconcentration and measurement of the concentrated analyte with an FID offers high sensitivity and a wide dynamic range (50 to 5,000 ppbC). A detection limit below 50 ppbC is possible, although the range of 50 to 5,000 ppbC is believed to encompass the normal range of ambient NMOC concentrations. The response versus concentration curves for all the alkanes and alkenes tested were colinear over the entire dynamic range; aromatic compounds, however, yielded somewhat lower response curves, as is typical with most hydrocarbon methods using cryogenic trapping.

Analyses of the 12 ambient samples collected in stainless steel canisters using this procedure yielded results within ±15 percent of analyses of these same samples using a gas chromatographic procedure. Analyses of four other samples collected in a Tedlar bag using the two methods yielded results differing by more than ±15 percent. This difference was thought to be due to sample container contamination. The precision of the new procedure was in the range of ±10 percent for replicate analyses of the same ambient sample.

The procedure is simple, rapid, cost effective, and can provide accurate data for measurement of nonmethane hydrocarbons in ambient air samples collected from sites both upwind and downwind of a source area.

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ABBREVIATIONS AND SYMBOLS

bp	boiling point
cm^3	cubic centimeter
EKMA	empirical kinetic modeling approach
FID	flame ionization detection
GC	gas chromatograph
HP	Hewlett Packard
ng	nanograms
NMOC	nonmethane organic compound
ppbC	parts per billion carbon
ppmC	parts per million carbon
TOC	total organic carbon

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Work on this project was performed by staff members of the Systems and Measurements Division of RTI under the direction of Mr. J. B. Tommerdahl, Division Director, and Mr. C. E. Decker, Assistant Director and Manager of the Environmental Chemistry Department. Dr. W. F. Gutknecht was laboratory supervisor for this program.

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SECTION 1

INTRODUCTION

Ambient nonmethane hydrocarbons and nitrogen oxides (NO_x) are primary precursors of ozone (O_3) and other oxidants, which are key constituents of photochemical smog. Current strategies for controlling these photochemical oxidants depend on nonmethane organic carbon (NMOC) abatement as the primary means of control. Measurement of ambient NMOC concentration provides essential input for photochemical models to determine the ambient hydrocarbon reductions required to achieve the national ambient air quality standard for ozone.[1,2]

Two general approaches to NMOC analysis are currently in use--"continuous" and "discrete" (sometimes called "grab sample") analysis methods. Continuous NMOC analyzers have shown limited reproducibility of data. This is partly due to the inaccuracies of substracting a methane response from total organic carbon (TOC) response to obtain a measure of the smaller nonmethane organic carbon, which is the usual mode of operation for a continuous analyzer. Furthermore, ambient TOC and CH_4 concentrations must be measured on broad, relatively insensitive ranges of the instrument to accommodate the frequent, wide excursions of the TOC and CH_4 concentrations. With good operational and quality control procedures, however, the analyzers can produce useful measurements at concentrations above 0.5 ppm$C$[3] and are therefore best suited for NMOC measurements at urban sites.

Discrete analysis methods provide NMOC data representative of samples collected over a set time period. One approach to analysis of discrete ambient air samples is to measure their constituent hydrocarbons using a sophisticated, multicomponent gas chromatographic (GC) analysis system. This approach can provide accurate and sensitive NMOC measurements. However, because of the high costs and difficulties involved, measurement of ambient NMOC by this method is limited to short-term (1- to 2-month) studies rather than year-round monitoring. The purpose of this study was to develop and evaluate a new

technique for measuring ambient concentrations of nonmethane organic compounds using cryogenic preconcentration and flame ionization detection. It is hoped that this technique may alleviate some of the problems encountered with other NMOC methods.

Accordingly, Research Triangle Institute (RTI) under contract to the Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency (EPA), Research Triangle Park, North Carolina, initially evaluated an experimental system built and used by McBride and McClenny.[4] Based on this preliminary evaluation, a new system was constructed and experimental conditions were optimized for measurement of NMOC either in the field or in the laboratory.

Detailed discussion of the experimental system, the sampling and analysis procedures, and the results of testing the system are described. In particular, Section 2 contains a summary and conclusions from the study; Section 3 contains recommendations for improvement of the method; Section 4 provides the description of the method, test apparatus, and operational procedures; Section 5 presents the experimental results; and Section 6 covers the quality control/quality assurance aspects of the study. A complete description of the operating procedures used for this method is given in Appendix A.

SECTION 2

SUMMARY AND CONCLUSIONS

A procedure for determination of gaseous nonmethane organic carbon in ambient air is described. This procedure involves cryogenic preconcentration of the NMOC and measurement of the revolatilized NMOC using flame ionization detection (FID).

A number of instrumental components of the system were optimized, as were several aspects of the system operation. The optimum cryogenic trap was a coil of chromatographic grade stainless steel tubing, 0.21 cm inner diameter and 120 cm in length. Either liquid oxygen or liquid argon can be used as a cryogen because neither traps methane. The trapped NMOC species were volatilized by warming the trap with hot water, and a six-port, two-position valve was used to direct the revolatilized sample into the FID. Ambient air can be sampled directly, although it is recommended that 3-hour integrated samples be taken in stainless steel canisters (or possibly Tedlar® bags) for subsequent analysis by the system. The system can be operated either onsite or at a central laboratory.

The system was tested with a variety of aliphatic and aromatic compounds. All of the aliphatic organic compounds tested followed the same response curve. Responses for toluene and benzene were 19 percent lower than those for the aliphatics. Xylene responses were found, however, to fall 50 percent below the aliphatic response. A dynamic range of 50 to 5,000 ppbC was attained with the detection limit below 50 ppbC. The method is free from humidity effects if the trap is not contaminated and can yield precisions of ±5 percent for single and multiple component gas standards and ±10 percent for actual ambient samples. Actual ambient samples were collected and analyzed using both the NMOC procedure and a gas chromatographic (GC) procedure. The two methods agreed within ±15 percent for 12 samples collected in stainless steel canisters. Four additional samples collected in a Tedlar® bag exceeded the ±15 percent range, apparently due to problems with the sample bag.

Further testing and refinement are necessary to obtain improved comparisons with manual GC analyses of ambient samples and to improve the method's efficiency with aromatic compounds.

SECTION 3

RECOMMENDATIONS

Several specific recommendations for further testing and refinement of this method became evident during our evaluation; the following offer promise of improved data quality:

- Further comparisons of ambient air sample analyses with gas chromatographic results should be performed to better establish the precision and accuracy of this method for samples collected both in bags and stainless steel canisters.

- Two modified Beckman 400s were tested for use as a detector for the NMOC method. Other types of total hydrocarbon analyzers probably could be used with suitable modifications, but no others have been tested. Therefore, evaluation of the suitability of other total hydrocarbon analyzers for this method should be performed. Included in such an evaluation of an alternative TOC analyzer should be such considerations as: extent of modification required; use of helium as the carrier gas; flow rates for stable FID operation; and modification of the analyzer to give equivalent responses to all the hydrocarbon species.

- An initial negative FID response occurred due to a temperature-induced pressure surge in the carrier gas if the hot water used to volatilize the NMOC sample was put on too quickly. This interferes with accurate integration since the NMOC peak occurs 30 seconds after the baseline disturbance. Proper technique can minimize this problem, but development of a simple, improved electrical resistance heating technique would solve the problems associated with the pressure surge and the inconvenience of using hot water.

- Inclusion of a capillary or substitution of 0.159-cm tubing in place of the 0.316-cm tubing between the six-port valve and the sample inlet of the Beckman, or use of a flow controller instead of the one-stage regulator, may help "dampen out" the pressure surge that hampers the hot water volatilization technique.

- Experiments with p-xylene have indicated that the lower FID response for aromatics might be inherent to their chemical properties in the flame. Further study of aromatics is warranted to make this method more universal in its detection.

- Experiments using the system shown in Figure 2 with a temperature-controlled, valve heating box and heating tape around sample lines may offer better recovery for aromatics contained in ambient samples.

- Helium was used as a carrier gas in this study. The suitability of using less expensive nitrogen as a carrier gas should be determined.

- Further studies of the effect of air-hydrogen ratios and flow rates on hydrocarbon responses are warranted to possibly minimize the reduced responses of aromatics and possibly to minimize the costs of the support gases used.

- An open tubular stainless steel trap was employed. Experimentation with packed traps may offer improved data quality if they result in reduced pressure surges or offer other advantages.

SECTION 4

DESCRIPTION OF METHOD, TEST APPARATUS, AND OPERATIONAL PROCEDURES

OVERVIEW

The principles upon which the method is based are relatively straightforward: An air sample is taken either directly from the ambient air at the monitoring site or from a sample bag or canister filled previously at the site. A fixed-volume portion of the sample is drawn at a low flow rate through a tubular trap cooled to approximately -185° C. After the fixed-volume air sample has passed through the trap, a flow of helium is flushed through the trap and into an FID analyzer that is modified to operate with a helium carrier. When the residual methane and oxygen have been cleared from the trap by the helium and the FID baseline becomes steady, the temperature of the trap is raised to approximately 80° C. The organic compounds collected in the trap revolatilize and are carried into the FID with the helium, resulting in a response peak or peaks on a chart recorder connected to the FID analyzer output. The area of the peak is integrated, and the integrated value is translated to concentration units via a previously obtained calibration curve that relates the integrated reading with known concentrations of propane. A detailed discussion of the analytical system, trapping procedure, and measurement procedure follows.

ANALYTICAL SYSTEM

The analytical system consisted of two major subsystems: a trapping system to collect and preconcentrate the sample and a total organic carbon (TOC) analyzer (a modified commercial flame ionization detector). The sample preconcentration system served two primary purposes. It trapped and concentrated the NMOC, and it allowed separation of methane and NMOC. The general system design, description of the major components, and trapping and measurement procedures are discussed in the following subsections.

General System Design

Figure 1 shows a schematic of the analytical system. This system was constructed from commercially available components in a modular design as shown in Figure 2. This system was designed to fit into a commercially available aluminum suitcase for easy transportation.

All tubing used for the system was 0.3175-cm (1/8-in) stainless steel connected with stainless steel fittings. Connections for vacuum and helium carrier gas were made through bulkheads on the panel of the modular system. Other connections were made directly to the six-port valve. The stainless steel tube between the FID and the six-port valve was kept as short as possible to avoid losses due to cooling, adsorption, and spreading of the sample peak.

It was also important to minimize the tubing and use of connectors between the valve and the sample trap to prevent sample losses due to cool, dead spaces. After assembly, the absolute pressure gauge was disconnected to prevent possible damage and the line to it was capped; the system then was pressurized to about 500 kPa (80 psig) and checked carefully for leaks. When the system was free of leaks, it was depressurized and the absolute pressure gauge was reconnected.

NMOC Trap--

Careful attention was given to the construction of the sample trap. The trap shown in Figure 3 was evaluated and showed quantitative trapping for most of the compounds tested. The trap was fabricated from a 120-cm length of 0.3175-cm (1/8-in) o.d., 0.21-cm i.d. chromatographic grade stainless steel tubing shaped to the dimensions shown in Figure 3. Alternative traps should be thoroughly evaluated for their efficiency before use. Thicker-walled and shorter traps have shown reduced trapping efficiency (Section 5). An open tubular trap was used instead of a packed trap since large changes in flow rate were observed with the latter when the trap was warmed for volatilization and measurement of the trapped NMOC. The trap was connected directly to the six-port valve to minimize line length between the trap and the TOC analyzer.

Liquid Cryogen--

Either liquid oxygen (bp -183° C) or liquid argon (bp -185.7° C) may be used for the cryogen; experiments have shown no difference in trapping effi-

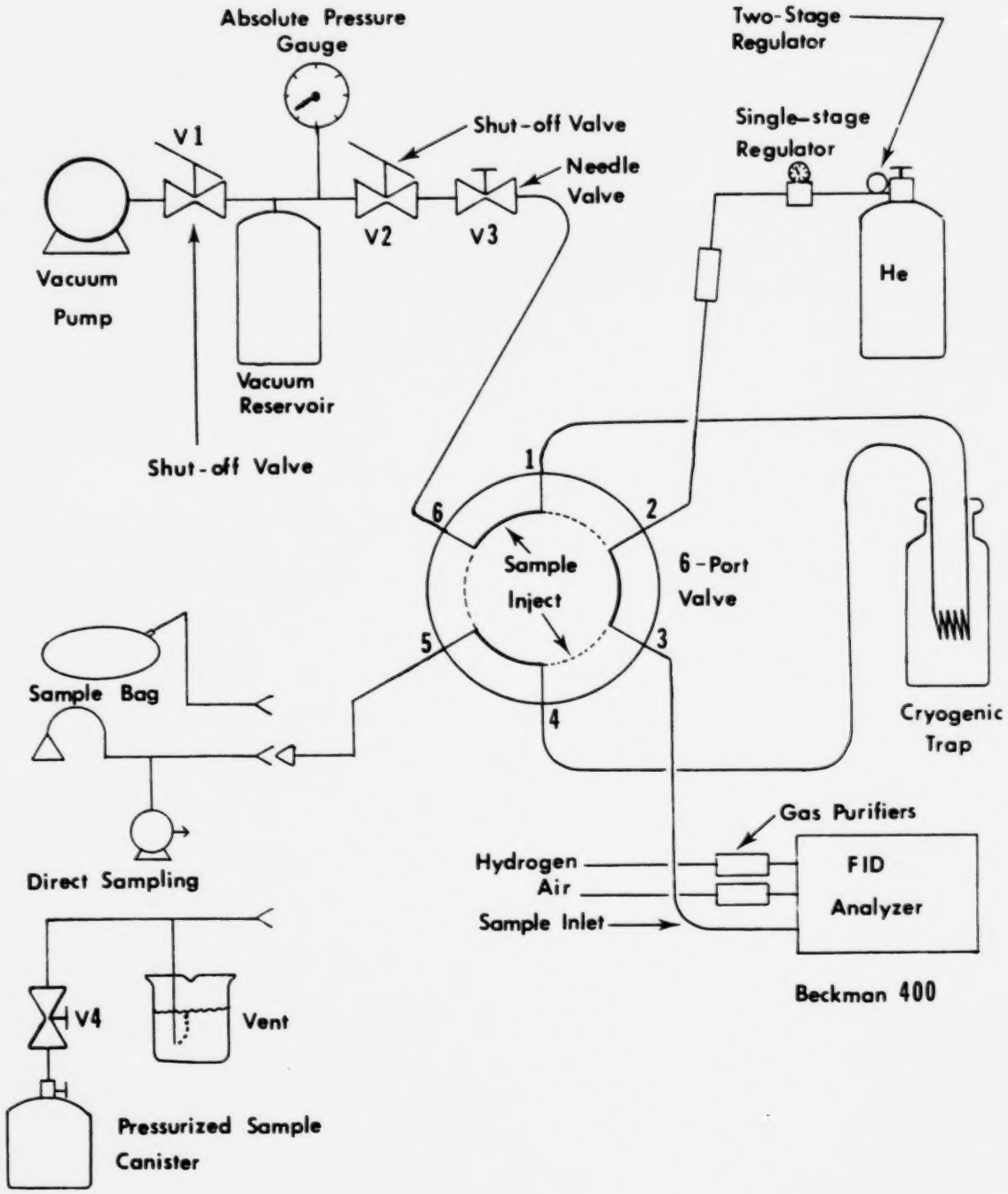

Figure 1. Schematic of analysis system showing three sampling modes.

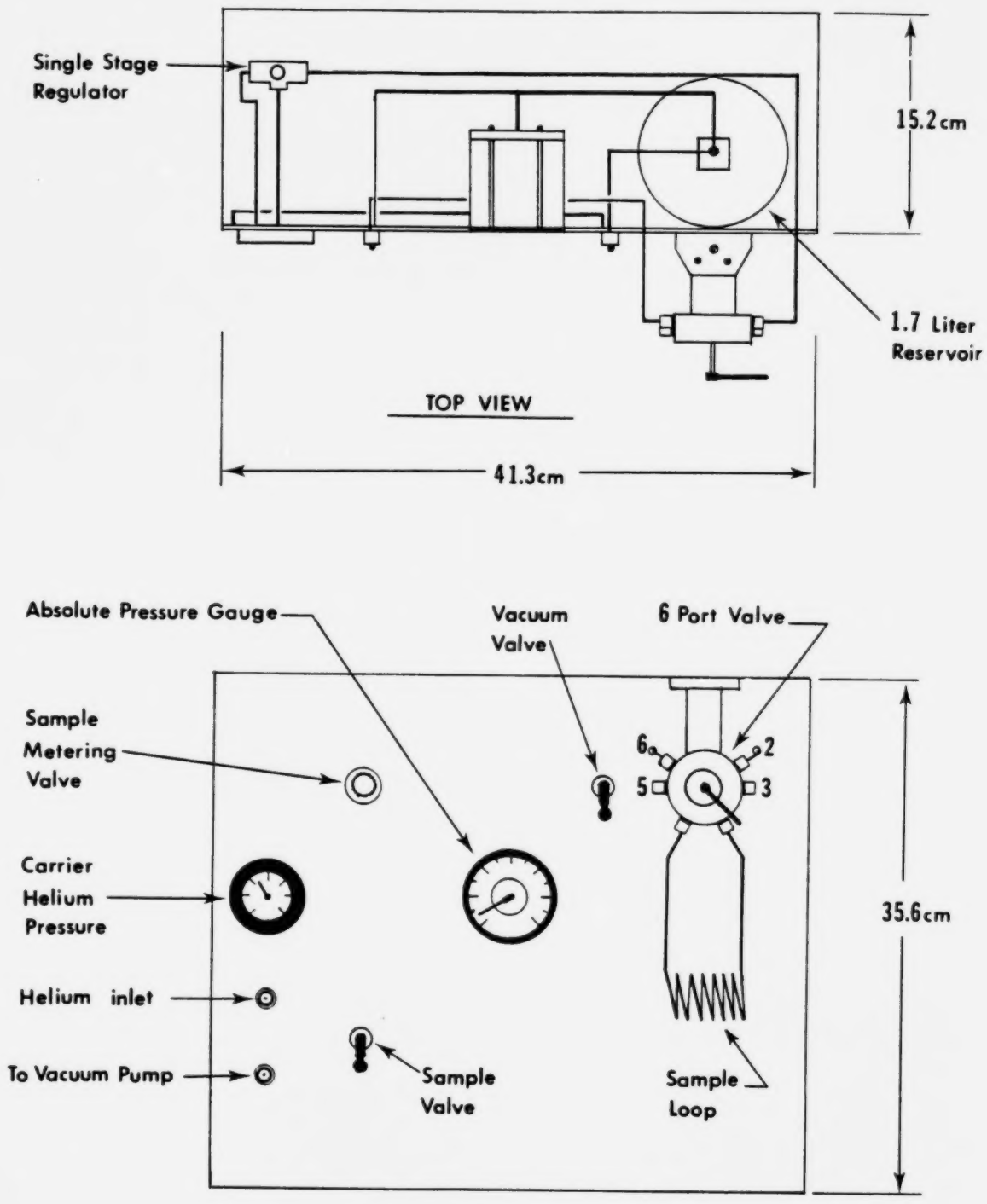

Figure 2. A modular design for the preconcentration system.

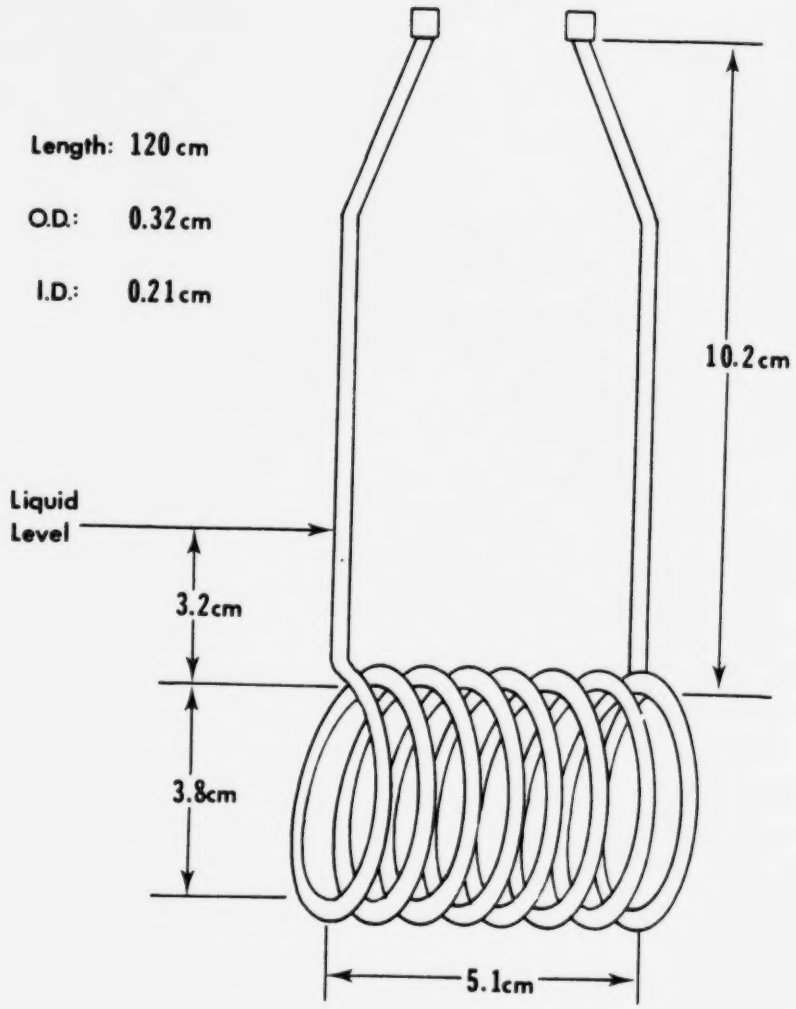

Figure 3. Sample trap.

ciency between the two cryogenic liquids. However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen (bp -195° C) cannot be used as the cryogen because its use results in condensation of oxygen and methane in the trap. The level of the liquid seemed to be important, so it was kept constant at a point that completely covered the trap coils.

Heat Source--

A hot water bath was used to volatilize the concentrated, trapped sample to facilitate integration of the NMOC response peak. Without application of an appropriate heat source, components of the sample fractionally distilled from the trap as it slowly warmed to room temperature, and a series of small, hard-to-integrate peaks resulted. This was particularly true for the heavy molecular weight C_7-C_{10} organic compounds. The water was heated above 75° C but not to boiling (100° C). A suitable heating source was a simple electrical immersion heater, which readily heated about 1 L of water to between 75° and 85° C. Poorer precision was obtained when the water was cooler. Heating the trap by direct connection of a low-voltage, high-current source to the trap (i.e., using the trapping tube as a heating element) may be a reliable alternative.

Carrier Gas--

Helium was used to purge the trap of residual methane and oxygen and also to carry the volatilized sample into the FID. The use of helium carrier gas altered the FID (Beckman Model 400) performance so that differences in responses of various hydrocarbon compounds were minimized. The carrier gas flow rate was optimized for adequate FID response with minimum transient effects when the valve was switched and the trap was warmed. The optimum carrier gas flow rate for this system was 76 ± 10 mL/min. To minimize the effects of fluctuating carrier gas flow rates resulting from variations in helium source pressure, a single-stage regulator was used on the helium carrier line in addition to the two-stage cylinder regulator. The secondary stage of the two-stage regulator was set at a pressure slightly higher than the pressure setting of the single-stage regulator so that the latter could function properly.

FID/TOC Analyzer--

Two modified Beckman 400 TOC analyzers were tested in this study. Other types of total hydrocarbon analyzers could be used with suitable modifications, but none have been tested. A schematic diagram of the Beckman 400 hydrocarbon analyzer is shown in Figure 4. The analyzer was modified by capping off the sample bypass line at the Swagelok tee from which the sample capillary originates to force the entire sample stream through the capillary. Helium was used as a carrier gas for the FID instead of air, which is used conventionally with the Beckman 400. The carrier gas flow was controlled by the auxiliary single-stage regulator on the helium line upstream of the six-port valve. The last alteration was a change of the hydrogen and burner air flow rates to hydrogen at 45 mL/min and burner air at 650 mL/min. With these modifications, the Beckman 400 yielded equivalent per-carbon responses for most hydrocarbons tested and response curves that were linear with concentration.

Data Recording System

During the course of the study, four different peak integrator/recorders were tested. These were: (1) a Linear integrating chart recorder (Model 252A); (2) a Spectra-Physics Minigrator; (3) a Hewlett-Packard 3352B data acquisition system; and (4) a Hewlett-Packard 3390A digital integrator/recorder.

The integrating chart recorder yielded linear responses within each voltage output range of the Beckman 400 tested. However, this recorder did not respond as expected when switching from one output range of the Beckman to another. This problem may have resulted from an inaccurate range attenuator or from a possible impedence mismatch. To deal with the problem, a separate calibration curve was prepared for each Beckman 400 voltage output range used.

For all of the integrators, careful setting of the zero-baseline was essential to the accuracy of the method. An initial negative FID response occurred if the hot water used to volatilize the NMOC sample was applied too rapidly, a condition apparently caused by some form of pressure surge. This negative baseline caused inconsistent integration by the Spectra-Physics Minigrator. The Minigrator is excellent if the peaks are symmetrical with no baseline shifts. The Hewlett Packard (HP) integrating systems suffered no such problems because their baselines could be set manually. Also, the HP integrating systems were capable of integrating unsymmetrical peaks accurately,

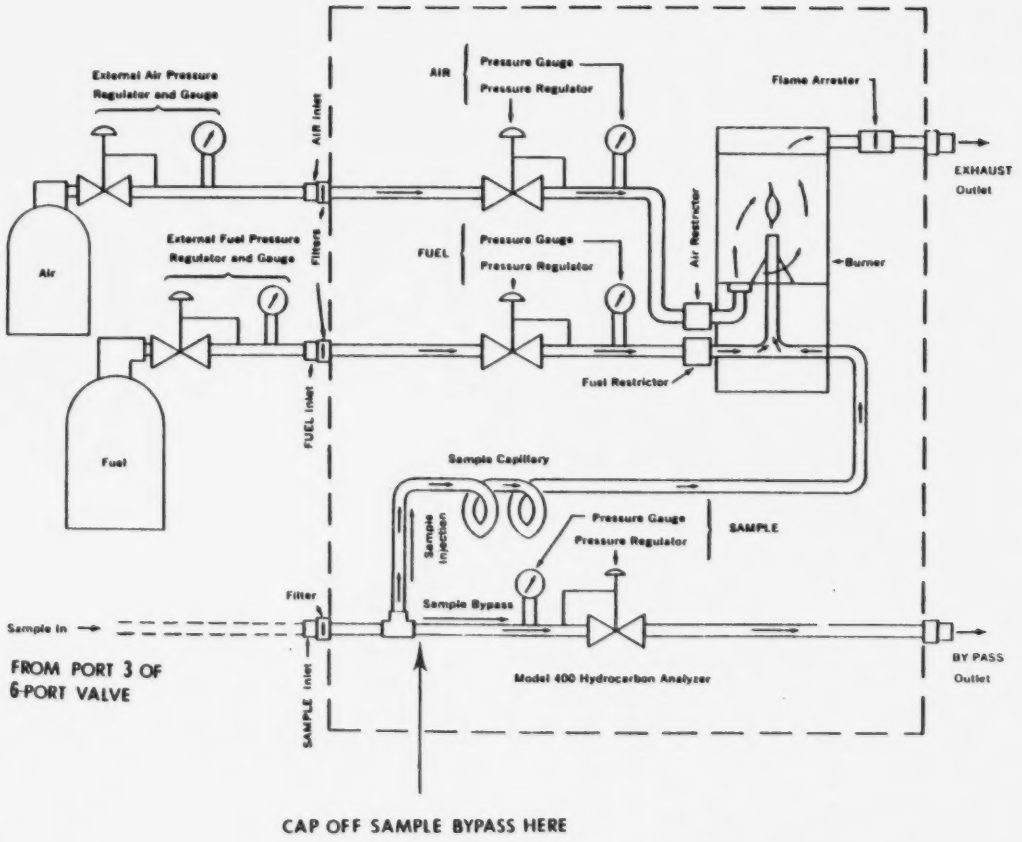

Figure 4. Schematic of Beckman model 400 analyzer showing modification.

compensating for baseline shifts, and peak trimming. Of the systems tested, the Hewlett Packard 3390A integrator was preferable.

Trapping and Measurement Procedure

The trapping and measurement procedures are described in the following subsections.

Trapping Procedure--

Ambient field samples (or calibration gas samples) were concentrated for analysis by passing a certain volume from the sample container through the cryogenically cooled trap into an evacuated reservoir of a known volume downstream from the trap (see Figure 1). The volume of sample taken was determined from the known volume of the reservoir (constant) and the observed change in pressure in the reservoir as measured by the absolute pressure gauge. This volume can be calculated by

$$V_s = \frac{\Delta P \; V_{res}}{P_a}$$

where

V_s = Volume of air sampled in standard cm^3,

ΔP = Pressure difference measured by gauge in mm Hg,

V_{res} = Volume of vacuum reservoir in standard cm^3, and

P_a = Ambient pressure in mm Hg.

In the system described, the reservoir volume (V_{res}) was 1,700 cm^3, ambient pressure (P_a) was generally about 760 mm Hg, and the pressure change (ΔP), accurately measurable with the gauge used, was 180 mm Hg (20 to 200 mm Hg). The volume of air sampled for these conditions is thus calculated as

$$V_s = \frac{180 \times 1{,}700}{760} = 403 \text{ cm}^3 \quad .$$

The actual reservoir volume was noncritical since it was constant throughout calibration and sample analysis; however, changing the sample volume changes the sensitivity of the method. Sample volumes of 200 to 500 cm^3 were evaluated and found to follow the same calibration curve (response vs. NMOC in nanograms of carbon). These sample volumes were also appropriate for typical ambient

NMOC concentrations. If the response peak obtained for a 500-cm^3 sample was outside the calibration range or off scale, a second analysis of a 250-cm^3 sample was made.

Measurement Procedure--

After a known volume of sample had been cryogenically trapped, the flow of helium was flushed through the cold trap and into the FID (TOC analyzer). When the residual methane and oxygen had been purged from the trap and the baseline of the FID response became steady, the liquid cryogenic bath was removed and replaced smoothly but not too quickly with a Dewar of hot water (approximately 80° C). The organic compounds collected in the trap revolatilized and were carried into the FID, resulting in a response peak or peaks on a chart recorder connected to the output of the TOC analyzer. The area of the peak was integrated, and the total NMOC integrated peak area was translated to concentration units using a previously obtained calibration curve. The shapes of the NMOC peaks were not reproducible, but the total peak areas were reproducible.

SAMPLING SYSTEM

A variety of integrating sample collection techniques can be used for the collection of ambient air samples. The most common devices for collection are precleaned, evacuated stainless steel canisters and Tedlar® or Teflon® bags. Tedlar® bags are usually preferred over Teflon® because the sturdiness of the bag seal results in fewer leaks. Also, Tedlar® bags have shown less background contamination after repeated cleaning than Teflon® bags.[5] The use of stainless steel canisters is preferred when analysis of bag samples cannot be accomplished within 3 hours after sampling.

Integrated, ambient air samples can be collected directly or from station manifolds over predetermined time periods at flow rates consistent with the desired integration time and the volume of the sample container. A detailed discussion of the sampling techniques used is given in Appendix A. Advantages of each container type and the sampling procedure are summarized in the following subsections.

Stainless Steel Canisters

Collection of ambient air samples in pressurized stainless steel canisters provides a number of advantages, including the following:

- Integration of ambient samples over a significant time period, e.g., 3 hours;
- Remote sampling and central analysis;
- Ruggedness and easy storage and shipping of samples;
- Low background (with proper cleaning); and
- Longer storage time between sampling and analysis.

Care must be exercised in selecting and cleaning the sample canisters to avoid losses or contamination of the samples. A detailed discussion of the techniques recommended to clean stainless steel canisters is given in Appendix A.

Sample Bags

Sample bags (Teflon® or Tedlar®) are simpler, more readily available, and less expensive than canisters; of the two, Tedlar® bags are preferable. Unlike canisters, however, bags cannot be cleaned with heat. Also, contamination from permeation into the bag or loss through permeation out of the bag may be significant problems. Bag samples must be analyzed within 3 hours of the time of collection and must be protected from heat and sunlight. Storing the sample bags in opaque containers such as cardboard boxes is recommended.[6] Samples collected in bags can be transferred into steel canisters to extend the storage period,[6] but this combines the potential problems of both types of containers.

Sampling Procedure

Figure 5 shows the schematic of a recommended sample collection system. A detailed discussion of the sample collection system is given in Appendix A. In summary, 3-hour integrated ambient air samples are collected in clean, stainless steel canisters or sample bags using a metal bellows pump in a sampling system designed to reduce the residence time of the ambient sample in the sample lines. Shorter residence time may reduce losses of higher molecular weight compounds by reducing the time available for them to become adsorbed on the surface of the inlet tubing. The sample auxiliary pump purges the

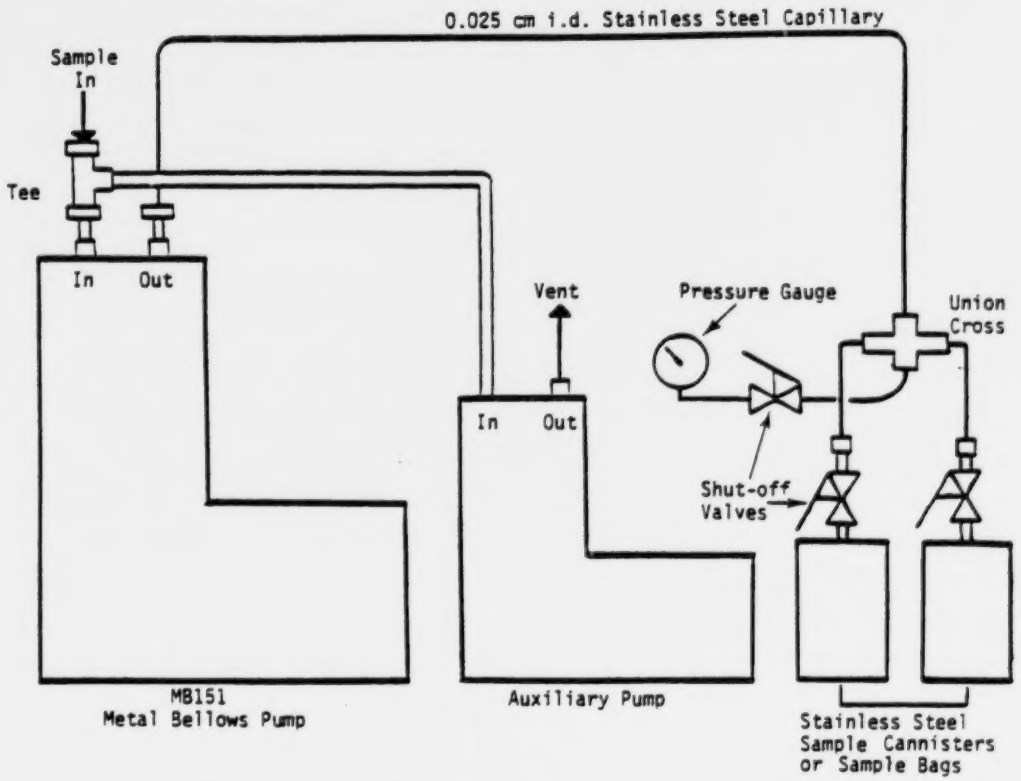

Figure 5. Sample system for collection of integrated field samples.

inlet manifold or lines with a flow of several L/min to minimize the sample residence time. The larger metal bellows pump (MB-151) takes a small portion of this sample stream and pressurizes it to fill the sample canisters. The capillary connecting the outlet of the metal bellows pump to the canisters is used to limit the flow into the canisters and must be cut to a length that provides the desired flow rate. This flow rate is chosen so that the canisters are pressurized to at least 1 atmosphere above ambient pressure (2 atmospheres absolute pressure) over the desired sample period. This final pressure facilitates transfer of the sample from the canister into the cryogenic trap.

SECTION 5

EXPERIMENTAL EVALUATION

EXPERIMENTAL APPROACH

Two prototype NMOC analysis systems were evaluated. The first prototype was delivered to RTI by EPA after construction and preliminary evaluation[4] by Dr. W. McClenny et al. of the U.S. Environmental Protection Agency. The second system was constructed by RTI in an effort to produce a portable unit of more optimized design. The RTI system included some minor changes to improve cryogenic trapping. Each system used a separate Beckman 400 TOC analyzer having the modifications described previously. Analytical parameters tested included response to various hydrocarbons, efficiency of separation of methane, effect of sample flow rate through the cryogenic trap, effect of sample volume, and effect of humidity. Other parameters including accuracy, precision, and linearity were also evaluated. Each system was used for part of the evaluation. The experiments performed with each system and the results obtained are discussed in the following subsections.

EXPERIMENTS PERFORMED WITH INDIVIDUAL PROTOTYPE SYSTEMS

EPA Prototype System

The experiments designed and performed with the EPA prototype system include:

- Evaluation of FID gas flow rate parameters,
- Evaluation of instrumental ranges (Beckman 400),
- Analysis of a methane standard,
- Optimization of sample flow rate through the cryogenic trap,
- Determination of effect of humidity,
- Determination of effect of changes in sample volume,

- Determination of response to different alkanes and alkenes,
- Comparison of two traps with different dimensions and determination of trapping efficiency with two traps connected in series, and
- Analysis of a C_2-C_9 multicomponent mixture for comparison with GC results.

RTI Prototype System

The prototype system built by RTI included an improved, thinner-walled 120-cm trap and was designed so that the six-port valve and stainless steel sample lines could be heated if desired (see Figure 2). Heating was used to minimize the losses of aromatics in the sample lines. After construction of the system, the following experiments were designed and performed:

- Determination of system responses to different aliphatics and aromatics,
- Determination of the effect of heating the trap to produce revolatilization,
- Determination of trapping efficiency and FID response for different hydrocarbons,
- Analysis of a C_2-C_9 multicomponent mixture for comparison with GC results, and
- Analysis of ambient air samples for comparison with GC results.

RESULTS AND DISCUSSION

EPA Prototype System

The results obtained for various analytical parameters evaluated with the EPA system using the original NMOC trap (3.2 mm o.d × 1.3 mm i.d × 100 cm long) are discussed below.

Gas Flow Rate Parameters--

The gas flow rates used for the flame ionization detector were:

Burner air	650 mL/min
Burner hydrogen	45 mL/min
Carrier helium	76 mL/min

Similar gas flow rates were also used for the preliminary studies done within the EPA laboratories. Small changes made in the hydrogen flow rates were found to have no significant effect on the response of the FID. The high burner air flow rate and the use of helium instead of air as a carrier gas are changes from normal Beckman 400 operating conditions. These modified conditions were selected in an attempt to alleviate the problem of differing response factors between different hydrocarbon species. The data below present the response factors relative to propane for three unmodified TOC analyzers using air, and those obtained for the modified Beckman 400 analyzer using helium.

Compound	Unmodified[7] MSA 11-2	Unmodified[7] Bendix 8201	Unmodified[8] Beckman 400	Modified Beckman 400
Methane	1.92	1.29	1.92	--
Propane	1.00	1.00	1.00	1.00
Ethylene	1.17	1.17	0.90	1.00
Acetylene	--	--	1.27	1.00
Propylene	0.93	1.02	0.90	1.00
Toluene	0.83	0.79	0.92	0.81
m-Xylene	0.60	0.51	--	0.50

Changes in the helium flow rates had significant effects on FID performance. When the helium flow rate was increased above 76 mL/ min, the baseline and hydrocarbon responses decreased and the pressure surge occurring after turning the valve increased. When the flow rate was increased to approximately 100 mL/min, the pressure surge became strong enough to extinguish the FID flame. When the helium flow rate was decreased below 76 mL/min, baseline response and hydrocarbon response both increased significantly. Also, the practice of turning the helium flow down at night to conserve helium was discontinued when it appeared that this practice caused deterioration of the FID electrode and an increase in baseline noise. No explanation for these effects was apparent. For these reasons, a helium flow rate of 76 mL/min was maintained at all times.

Beckman 400 Ranges--

The Beckman analyzer provides both a front panel range (i.e., attenuator) control and an internal, full-scale output voltage selector. An appropriate combination is necessary to obtain an adequate output level for accurate integration. The 10-mV full-scale output of the Beckman 400 was chosen since it was compatible with both the strip chart recorder and the integrator used. The integrator must be electrically compatible (e.g., input voltage and impedance) with the output signal of the TOC analyzer so that sufficient resolution is available at low concentrations without overranging at high concentrations.

Range selector controls on both the integrator and the TOC analyzer did not provide accurate range ratios. Therefore, individual calibration curves were prepared for each range. The TOC analyzer range X100 provided linear response from 150 ppbC beyond 2,200 ppbC, with a slight deviation from linearity below 150 ppbC. Although FID response is usually linear, these results indicated a significant nonlinearity below 150 ppbC. No explanation for this nonlinearity was apparent. The range X1000 provided a higher degree of linearity from 2,400 ppbC to 5,000 ppbC, but using this range rendered the system less sensitive below 300 ppbC. Setting the zero-baseline of the integrator was also very important to the method's accuracy.

Effect of Sample Flow Rate--

The effect of sample flow rate through the cryogenic trap on trapping efficiency was evaluated using a standard mixture of methane, ethane, propane, ethylene, and acetylene and ethylene alone (Scott cylinders A-7580, BAL-328) (see Table 1). Identical volumes of each gas were sampled at flow rates from 16 to 72 mL/min. These different flow rates appeared to have no significant effect on trapping efficiency. The variation of responses over these sample flow rates was 4 percent for ethane and 3 percent for ethylene, respectively. A sample flow rate of 45 mL/min was used throughout the study, unless stated otherwise.

Analysis of Methane--

Measurement of 9.56 ppmV NBS methane repeatedly gave no NMOC response. This finding ensured that methane was not trapped at liquid argon or oxygen temperatures.

TABLE 1. COMPRESSED HYDROCARBON CYLINDERS USED IN THIS STUDY

Cylinder	Contents
Scott B-237	19.9 ppmV propane in HCF air
Scott B-1519	9.82 ppmV ethane, 10.4 ppmV propane and 9.67 ppmV butane in nitrogen
Scott A-7580	1.86 ppmV ethane, 1.95 ppmV ethylene, 1.91 ppmV propane, 1.27 ppmV acetylene and 2.02 ppmV methane in nitrogen
Scott BAL-328	10.0 ppmV ethylene in nitrogen
Scott BAL-339	9.91 ppmV propylene in nitrogen
Scott A-5428	9.72 ppmV butane and 9.69 ppmV isobutane in nitrogen
Scott A-2910	9.90 ppmV butane and 10.1 ppmV trans-2-butene in HCF air, 25 ppmV ethane
Scott BAL-299	15.0 ppmV ethylene in nitrogen
Scott A-2735	9.74 ppmV acetylene and 9.21 ppmV n-pentane in nitrogen
Scott B-572	10.2 ppmV benzene in nitrogen
Scott B-1978	8.50 ppmV toluene in nitrogen
Airco LL 4451	23.4 ppmV p-xylene in nitrogen
Scott XA-8139	9.84 ppmV benzene and 8.23 ppmV ethylbenzene in HCF air
Scott B-1944	7.33 ppmV m-xylene in nitrogen
NBS-SRM	9.56 ppmV methane

Effect of Humidity--

The effect of water vapor on the analytical system was also studied. Water could have several possible effects, including clogging the cryogenic trap, increasing or decreasing trapping efficiency, or causing a shift in the baseline. The water vapor content of the test gas mixtures was controlled by mixing the sample with known amounts of clean air that had been passed through a bubbler filled with deionized water at a known temperature. The water vapor levels achieved varied from 15,000 to 30,000 ppm. Humidity experiments were carried out with both Scott mixtures (A-7580) and ethylene (BAL-308). As shown in Figure 6, no significant difference (±5 percent) was found between the dry and humidified Scott mixture (A-7850) over a wide range of concentrations. In addition, experiments with humidified ethylene sample showed no deviation beyond ±5 percent from the calibration curve of dry ethylene.

No significant reduction in flow rate through the cryogenic trap was observed when samples containing high moisture content were analyzed, demonstrating that clogging was not a problem. However, in some cases of high moisture content, an unusually broad peak was seen. In other cases, unusually long tailing tantamount to a slight baseline shift was observed. These effects were due to contamination in the trap, since the effects disappeared after thorough cleaning of the trap and lines. At high moisture content, water apparently displaces polar contaminants from the trap and releases them into the FID, causing an unusually broad peak or long tailing. To eliminate this problem, the cryogenic trap and stainless steel lines had to be cleaned periodically by heating with a hot air blower while keeping the six-port valve in the injection position and maintaining the helium flow. The cleanliness of the system was then checked by analyzing clean air that had been bubbled through deionized water. If no unusual peaks or long tailing (more than one minute after any expected hydrocarbon background response) were observed, the system was considered ready for test sample analysis. It was concluded from these studies that water had a minor effect on the analytical method when the system was free from contamination.

Effect of Sample Volume--

The Scott mixture (A-7580) was used to study the effect of variation in sample volume. The calibration line shown in Figure 7 was first obtained by

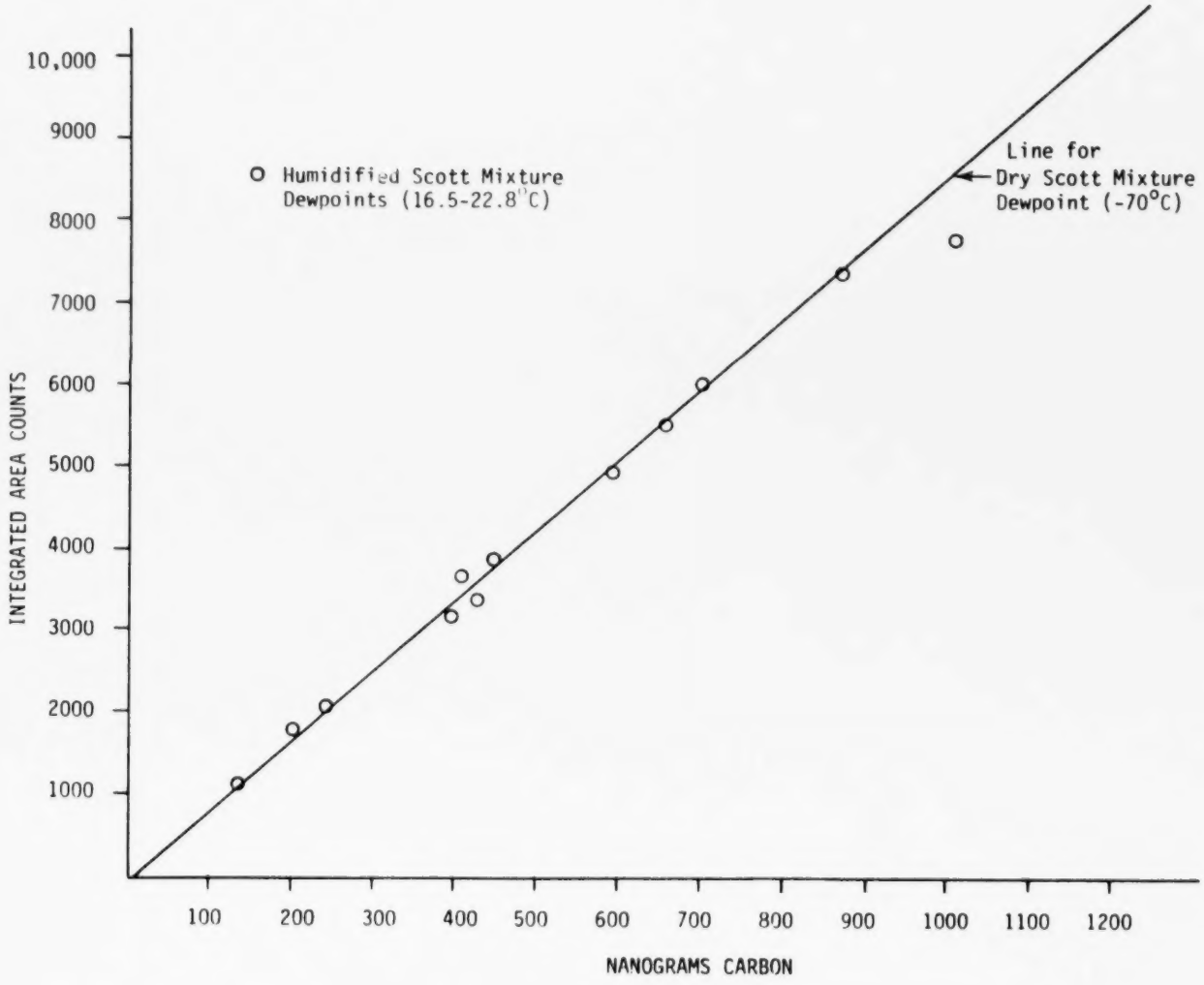

Figure 6. Effect of humidity on Scott A-7580 hydrocarbon mixture.

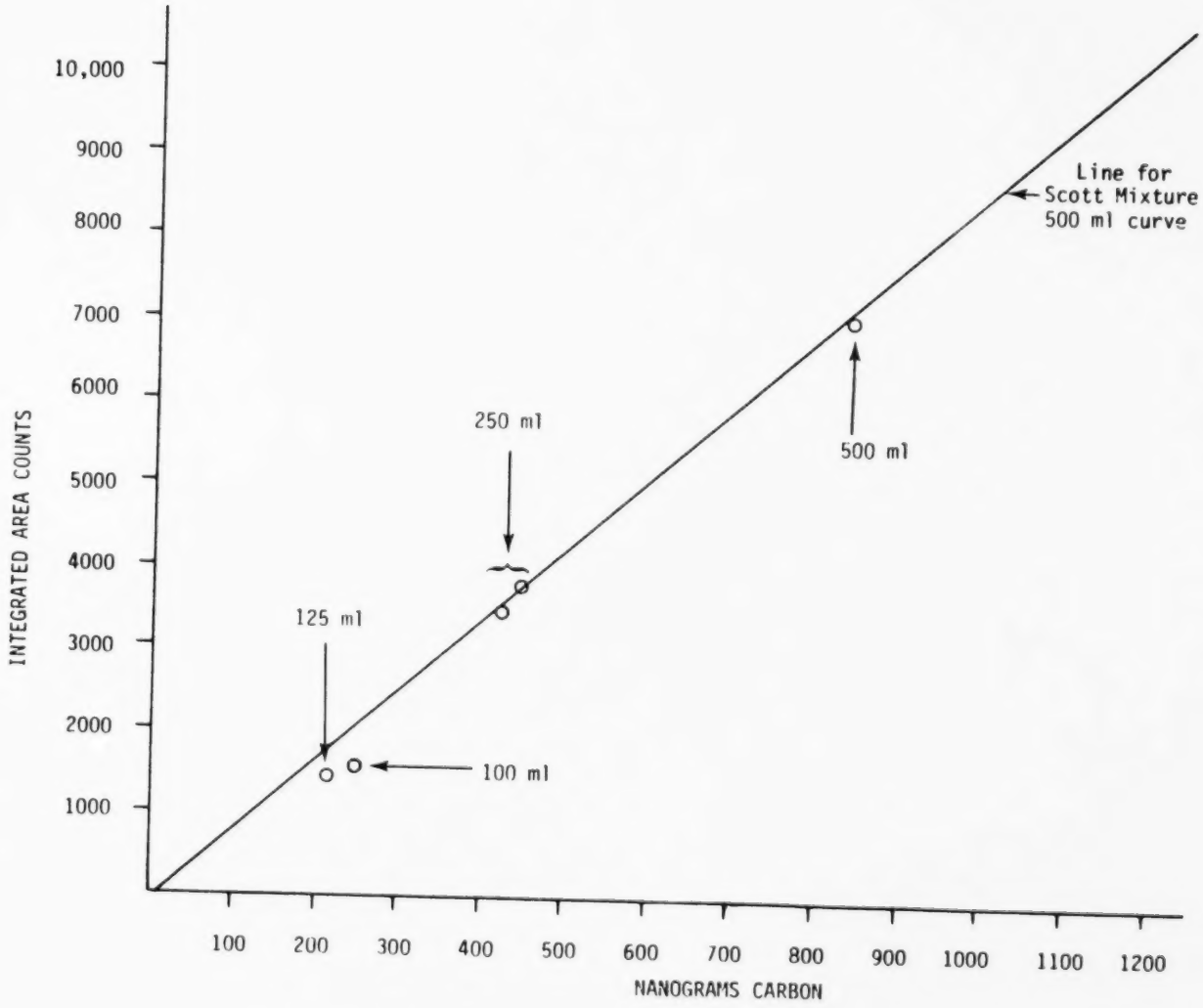

Figure 7. Study of sample volume effect using Scott A-7580.

trapping sample volumes of 500 mL for different concentrations of the Scott mixture. These different concentrations were obtained by diluting the Scott mixture with varying amounts of clean air. Next, samples less than 500 mL in volume were trapped. Figure 7 shows that points based on responses for sample volumes of 250 mL fell exactly on the calibration line. However, the responses obtained for sample volumes less than 250 mL, namely 125 mL and 100 mL, were significantly lower, i.e., 14 percent and 27 percent, respectively. These results indicate that sample volumes between 200 mL and 500 mL are acceptable. If the response peak obtained for a 500-mL sample turns out to be outside the calibration range or off scale, a second analysis of a 250-mL sample can be carried out.

Responses to Various Hydrocarbons--

Typical responses of the analytical system to various hydrocarbons are presented in Figure 8. As Figure 8 shows, most of the compounds tested, except for ethane and ethylene, followed the same calibration curve. Ethane (bp -90° C) showed a marked deviation at 238 ng (a 500-mL sample of 970 ppbC). Ethylene (bp -103° C) showed reduced response over its entire range. It was later found that reduced response for ethane and ethylene was due to incomplete trapping with this EPA system. Regression analysis excluding ethane and ethylene gave a correlation coefficient >0.99.

Comparison of the Trapping Efficiencies of Various Traps--

The original NMOC trap used in the EPA system was constructed from a single piece of chromatographic grade stainless steel tubing of 3.2 mm o.d. × 1.3 mm i.d. × 100 cm long. It was thought, however, that thinner-walled material would transfer heat out of the trap more efficiently and would improve the efficiency of trapping of ethylene and ethane. Therefore, a new trap was constructed with a thinner-walled stainless steel tubing having dimensions of 3.2 mm o.d. × 2.1 mm i.d. × 100 cm. The new 100-cm trap was initially tested with various concentrations of propylene and yielded a response 15 percent higher than the response obtained with the original NMOC trap. Ethylene gave a response 50 to 60 percent higher than the response obtained with the original trap and, in fact, ethylene followed the calibration line obtained with the other compounds up to about 1,500 ppbC. Above 1,500 ppbC, the response of ethylene began to fall below the calibration line. It was thought that

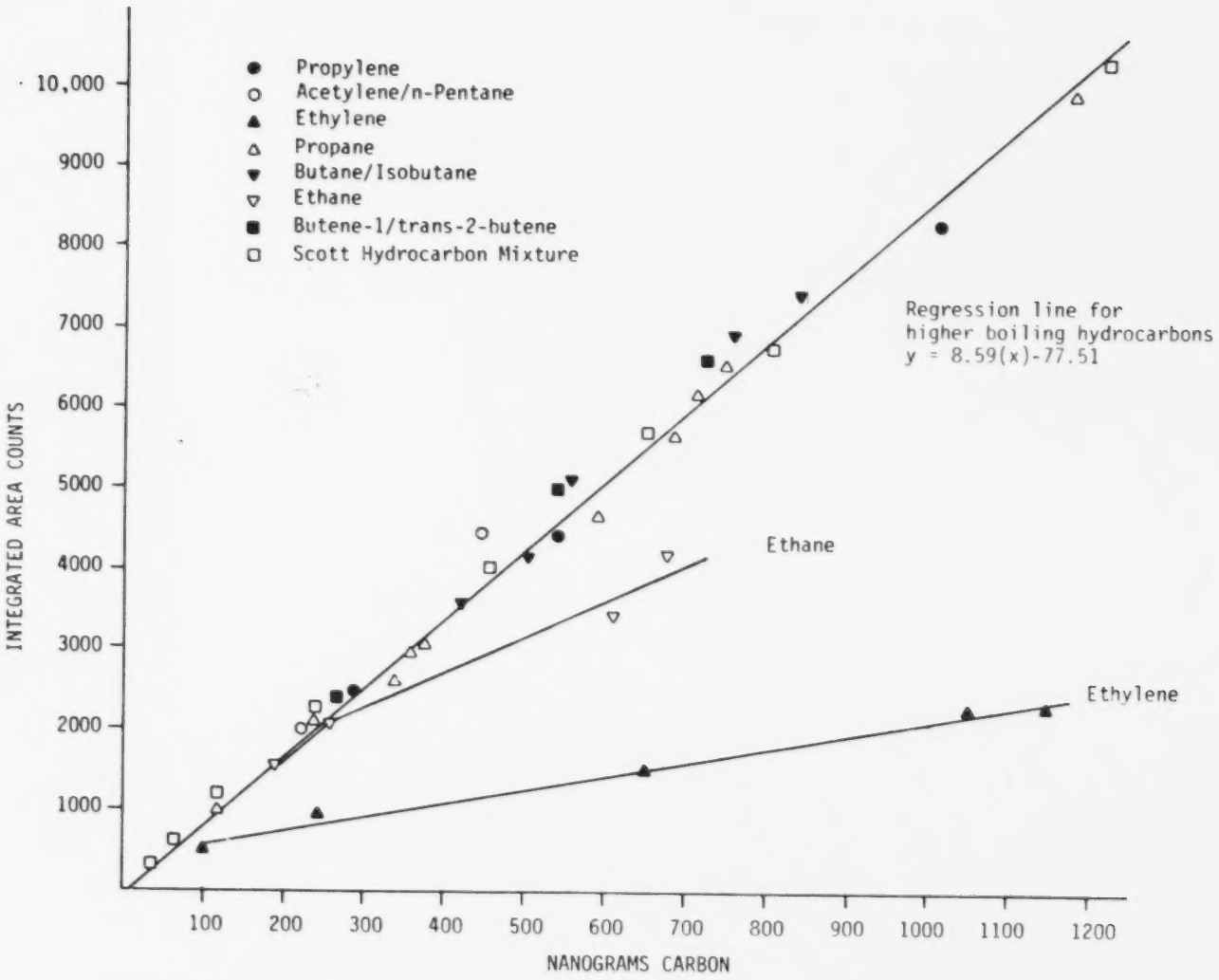

Figure 8. Hydrocarbon responses for the EPA prototype system with original sample trap.

increasing the length of the thin-walled trap would increase trapping efficiency of the low boiling compounds (ethane, ethylene, and acetylene) at higher concentrations (>1,500 ppbC). A new, 3.2 mm o.d. × 2.1 mm i.d. × 120 cm trap was constructed and tested using ethylene and propane. Both of these compounds showed the same response over a range of 1,200 to 3,000 ppbC. The response curves obtained for propane for the new 120-cm trap and the original EPA 100-cm trap are shown in Figure 9. The results indicate that the propane response curve was 15 percent steeper for the 120-cm trap compared to the propane response on the original 100-cm trap. (A t-test indicated that the slopes were different at the 95-percent significance level.) The reason for the 15-percent increase in response for propane with the new 120-cm trap is unknown.

To determine the reasons for the decreased efficiency obtained for ethylene and ethane in the original trap, an experiment was performed wherein the original trap and the new 100-cm trap were connected in series, with the old trap placed first in the sample stream. The fractions of the sample collected by the two traps were determined by first cyrogenically cooling both traps, then removing the cryogenic bath from the trap nearest the FID and, finally, by removing the cryogenic trap from the second trap. During seven experiments with ethylene, the original trap consistently collected only about 42 percent of the sample. The new 100-cm trap collected the remaining 58 percent. A subsequent experiment with 2,000 ppbC propane showed that all the propane sample was collected in the original trap and none was collected in the new trap. Also, the new traps (100-cm and 120-cm) tested alone gave the same response for propane and other compounds indicating that propane and higher molecular weight compounds were efficiently trapped in both traps.

The above experiments suggest that the original trap is inefficient for the collection of the low boiling compounds such as ethylene, and a thinner-walled, 120-cm trap (shown in Figure 3) is required to determine the ambient NMOC concentrations of these light compounds.

Analysis of C_2-C_9 Multicomponent Mixture--

A C_2-C_9 multicomponent mixture (Table 2) determined by GC-FID to contain 268 ppbC NMOC was analyzed using the EPA NMOC system. A value of 305 ppbC was obtained using regression analysis with reference to a standard propane calibration. No special heating of the trap was used to volatilize the sample

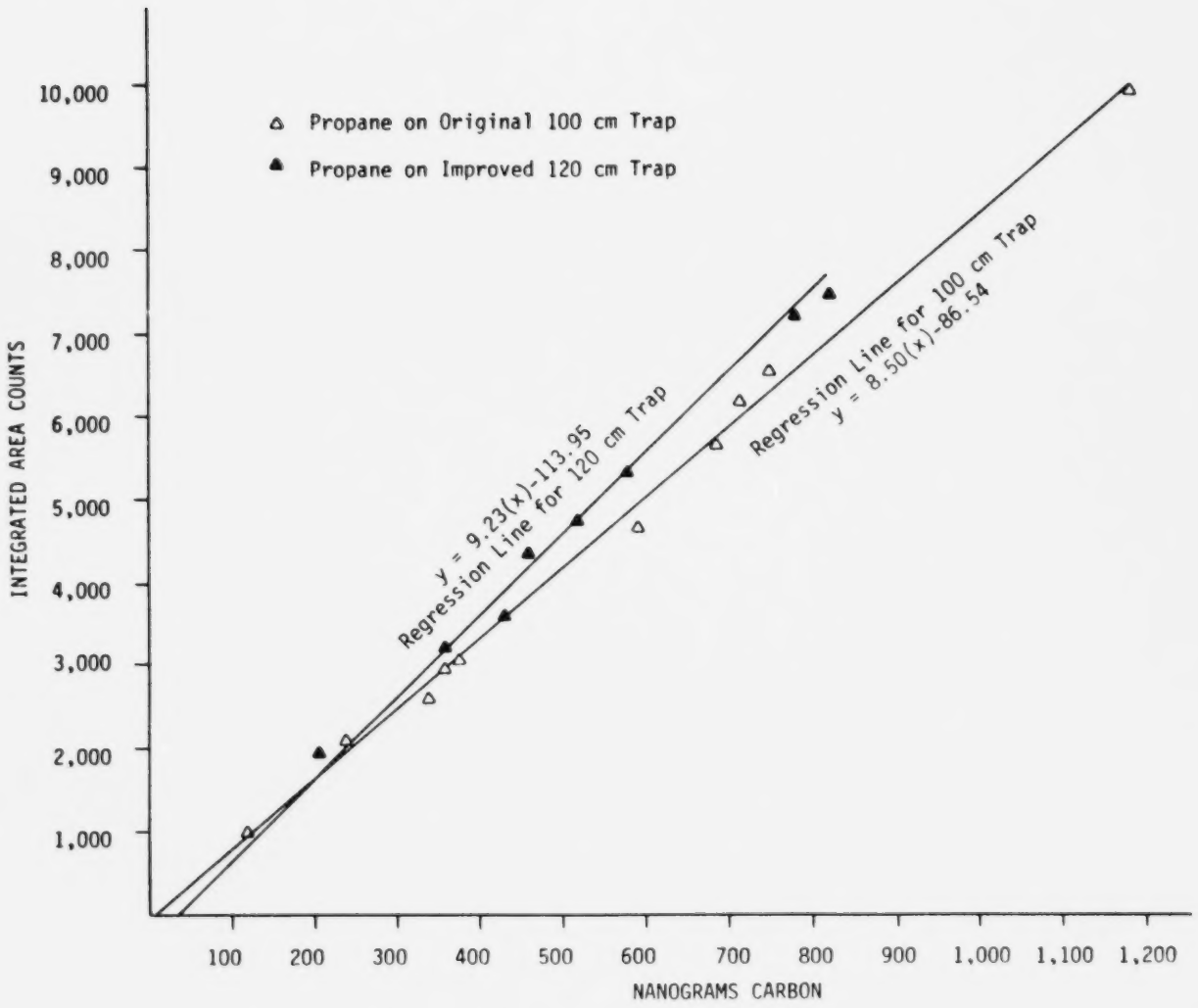

Figure 9. Comparison of original trap (100 cm) with the improved trap design (120 cm and thinner-walled).

TABLE 2. C_2-C_9 MULTICOMPONENT MIXTURE GAS CHROMATOGRAPHIC ANALYSIS[a]

Compound	Concentration (ppbC)
Ethane	19.4
Ethylene	21.1
Propane	21.2
Propylene	18.4
n-Butane	22.8
1-Pentene	26.1
2-Methylpentane	17.2
3-Methylpentane	17.5
1-Hexene	17.6
Benzene	21.0
Toluene	20.5
o-Xylene	16.5
n-Propylbenzene	14.2
1,2,4-Trimethylbenzene	14.2
Total	267.7

[a]GC analyses were performed by the Gas Kinetics and Photochemistry Branch of the Environmental Sciences Research Laboratory, Research Triangle Park, NC.

during the experiment; i.e., volatilization occurred through absorption of heat from room air.

RTI Prototype System

After its construction (see Figure 1), the RTI prototype system was tested to determine response to various aliphatic and aromatic compounds, trapping efficiency, FID response to different hydrocarbons, and effect of trap heating on recovery of the trapped samples. The sample volume, gas flow rates, sampling rate, and TOC analyzer output ranges used were those determined to be satisfactory with the EPA system. A thin-walled, 120-cm NMOC trap was used with the RTI system throughout the study. After the evaluation of the various parameters described, 16 ambient samples collected in Tedlar® bags and stainless steel canisters were analyzed with both the RTI NMOC system and a gas chromatographic procedure. The results obtained for the various experiments conducted with this system are discussed in the following subsections.

Hydrocarbon Responses--

Response of the analytical system to different carbon compounds was evaluated using 500-mL samples of a variety of different standard, aliphatic, and aromatic compounds. Figure 10 shows that all the aliphatic hydrocarbons tested, including ethane and ethylene, followed the same calibration line with even less "scatter" than with the EPA system; correlation coefficients were >0.99. Typical response lines for the aromatics tested are illustrated in Figure 11. The responses for toluene and benzene-plus-ethylbenzene are approximately 19 percent lower than the aliphatic responses. The xylene responses are about 50 percent lower than the aliphatic responses. Since these aromatic compounds have relatively high boiling points, their low responses are not related to the inefficient trapping problems observed for ethylene and ethane with the trap used in the EPA system. In fact, the trapping efficiency for these compounds was found to be 100 percent using two traps in series as described earlier.

Several possible reasons for the low responses of these species were considered, including: (1) these high molecular weight aromatics are considered "sticky" compounds and may be lost in the valve and in sample lines; (2) these compounds might not be readily volatilized from the cryogenic trap

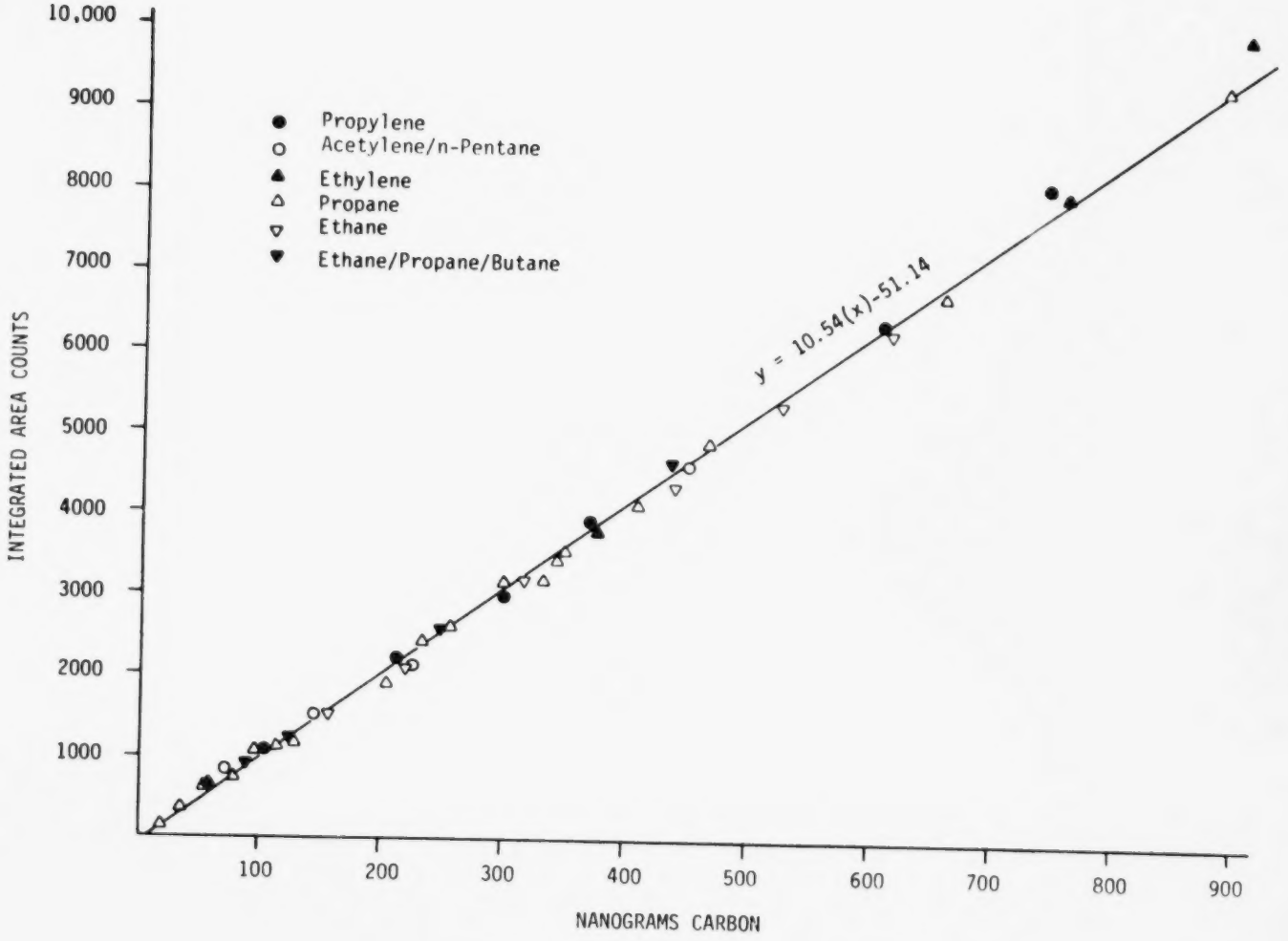

Figure 10. Aliphatic hydrocarbon responses for the RTI prototype system.

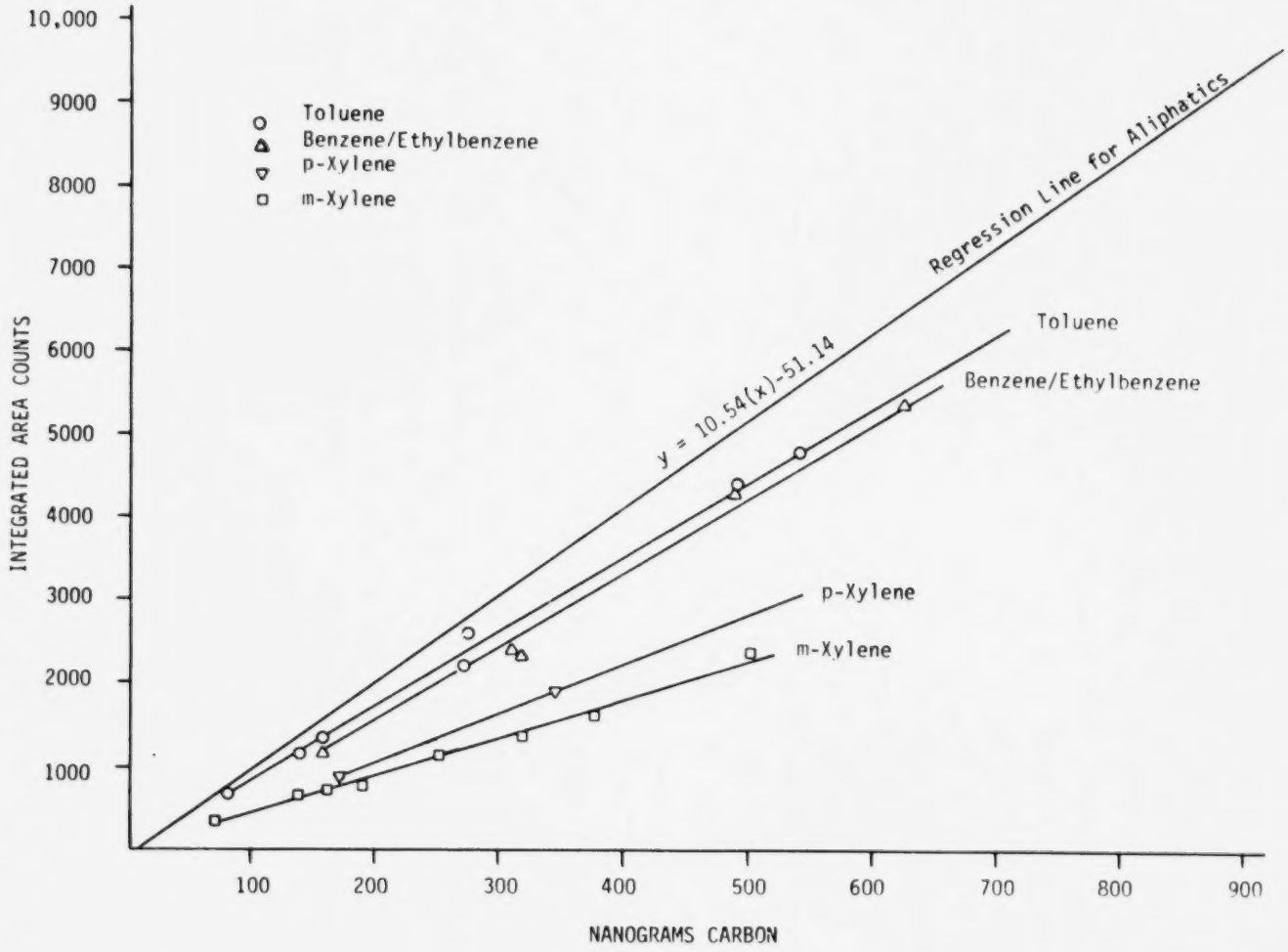

Figure 11. Aromatic hydrocarbon responses for the RTI prototype system.

and may slowly bleed off as a part of the background; and (3) the flame responses may be low for aromatics with this type of continuous TOC analyzer. Experiments were designed and performed to test the above possibilities, and the results are discussed in the following sections.

Hot Water Volatilization of Trapped Samples and Effect of Heating on Aromatics--

To achieve better release of the aromatic hydrocarbons and to obtain a more accurate analysis, the trap was heated upon removal of the cryogenic bath. The stainless steel tubing and the six-port valve were also heated with electrical heating tape to minimize losses in the sample lines. Heating the trap facilitates integration of the NMOC response peak by quickly volatilizing the sample, which results in sharp, easily integrated peaks. Without using heat, components of the revolatilized sample fractionally distill from the trap, and a series of small, broad, and hard-to-integrate peaks results.

Two methods of heating the trap were tested. One method that showed promise was using the stainless steel trap itself as a heating element. The ends of the trap were insulated from the valve with Teflon® fittings and a low voltage, high current source was connected to the ends of the trap. The 120-cm trap had a resistance of about 0.3 ohms and was connected to a low voltage a.c. source. This combination heated the trap too slowly, though the FID response showed complete freedom from the negative response and shifting baseline problems that were encountered later with hot water volatilization. A higher voltage source could possibly improve the heating process. However, it would be very important to use liquid argon rather than liquid oxygen as the cryogen to prevent possible ignition of the wiring insulation by a spark at a loose contact point.

The use of hot water to volatilize the sample was also investigated since this method would be easier to use. Earlier experiments with 40° to 50° C water yielded very poor precision. However, better results were obtained with water heated below boiling to 75° to 85° C.

The effect of heating on the responses of hydrocarbons (both aliphatics and aromatics) was investigated. The system responses to propane, toluene, and p-xylene were determined with and without hot water volatilization. The responses were identical. If efficiency or rate of release was a problem, the

use of a higher release temperature should have given rise to a larger response. A 20- to 30-percent higher response was obtained, however, with ambient air samples when hot water was used to cause volatilization. The reasons for the identical response for toluene and p-xylene with and without hot water and the significant difference in responses for ambient samples are unknown at this time. Further work is warranted.

Determination of FID Response--

To determine the FID response to p-xylene, an experiment was performed involving direct syringe injection of samples of p-xylene and an ethane/propane/butane mixture (as a reference) into the flame. The distance between the injection port and FID entrance was minimized (45 cm) to avoid losses on tubing walls. Both of these cylinder gases were prepared in a balance gas of nitrogen. The results for two different concentrations (704 and 1,030 ppbC) showed the response of p-xylene to be 30 percent lower than that of the aliphatic mixture in both cases. The 30 percent lower response of p-xylene is apparently due to the difference in flame response. This would explain 30 percent of the 50-percent difference found between p-xylene and aliphatic responses when using the total analytical system. The remaining 20 percent may be due to losses in sampling lines.

Analysis of a Multicomponent Mixture--

A laboratory-prepared, C_2-C_9 multicomponent mixture (see Table 2) determined by GC-FID* to contain 268 ppbC NMOC was analyzed using the RTI NMOC system. A value of 290 ppbC was obtained with hot water volatilization using regression line analysis of the results in reference to a standard propane calibration.

Analysis of Ambient Samples--

A series of 16 ambient samples collected in either Tedlar® bags or stainless steel canisters was analyzed using both the RTI prototype system and gas chromatographic procedures. The results from the samples collected in stainless steel canisters are shown in Table 3. The results from the ambient air samples collected in Tedlar® bags were inconclusive due to probable contamina-

*GC analyses were performed by the Gas Kinetics and Photochemistry Branch of the Environmental Sciences Research Laboratory, Research Triangle Park, NC.

TABLE 3. COMPARISON OF NMOC CONCENTRATION IN AMBIENT SAMPLES COLLECTED IN STAINLESS STEEL CANISTERS AND ANALYZED BY NMOC METHOD AND GAS CHROMATOGRAPHY

Sample No.	Date	GC analysis (as NMOC) (ppbC)	NMOC analysis (ppbC)	RSD[a] NMOC (%)	NMOC-GC (ppbC)	Percent error[b]
1	1/9/81	846	929	11	+ 83	+ 9.8
2	1/12/81	380	500	12	+120	+31.6
3	1/13/81	945	984	2	+ 39	+ 4.1
4	1/14/81	120	175	6	+ 55	+45.8
5	1/14/81	129 120	188 ---	10	+ 59	+45.7 +56.7
6	1/16/81	390	437	3	+ 68	+12.0
7	1/16/81	769	982	6	+213	+27.7
8	1/20/81	533	469	1	- 64	-12.0
9	1/20/81	328	365	2	+ 37	+11.2
10	1/20/81	223	252	9	+ 29	+13.0
11	1/20/81	549	469	12	- 80	-14.6
12	1/27/81	443	422	11	- 21	- 4.7
					Mean + 45	Mean +17.4

[a]Relative Standard Deviation of NMOC Results (RSD) = $\frac{\text{Standard deviation}}{\text{Mean}} \times 100$.

[b]Percent Error = $\frac{\text{NMOC result - GC result}}{\text{GC result}} \times 100$.

tion and are not presented here. However, it can be said that results of comparison analyses of the four samples collected in Tedlar® bags averaged 34 percent lower for the RTI prototype system than the GC system.

Twelve comparison analyses with samples collected in stainless steel canisters showed the test NMOC method to average 17.6 percent higher than the GC method, with 8 out of the 12 analysis results falling within ±15 percent. Careful precautions were taken to prevent pressurization of the sample trap when the sample was being removed from canisters. Consequently, there were no real differences in the analysis procedures for canisters and bags. However, a problem was encountered with the sample canisters during the course of these comparison studies that may account for much of the difference in NMOC observed between these two techniques. A very large contaminant peak appearing in the C_8-C_9 portion of the GC chromatogram was observed for many of the analyzed samples collected in canisters. This peak was due to a canister contaminant since it was not observed in ambient air samples injected directly into the GC system. During the canister sample collection, ambient air is routed through a Metal Bellows (MB-151) pump into the canister. The canisters are flushed and then filled to a pressure of 40 psi (275 kPa) above ambient. As the pressure in the canister exceeds 15 to 20 psi (100 to 140 kPa), the pump and sample begin to warm. At 40 psi (275 kPa), the pump and sample canister are quite hot to the touch. It was this temperature increase that probably caused the release of adsorbed contamination in the pump or sample canister. GC analyses were performed almost immediately after collection, and the large contaminant peak was observed. After storage for 1 hour, the magnitude of this peak decreased considerably. Although the peak's magnitude had decreased, it can be conjectured that some of this component or other components initially masked by this component's large signal were measured with the RTI NMOC system when this measurement was performed after the GC analysis. The amount measured cannot be estimated; however, one should note that the GC analyses results, which excluded the large peak from the NMOC calculation, were generally low with respect to the new NMOC technique.

Precision for these ambient samples using the NMOC technique was generally ±10 percent for replicate analyses of the same sample.

SECTION 6

QUALITY CONTROL/QUALITY ASSURANCE

Various procedures and tests were carried out in an effort to improve data quality, including careful calibration, daily testing for calibration shifts, comparison of analyses of ambient samples to gas chromatographic results, and measurement of system blanks taken with dilution air and carrier gas.

SYSTEM BLANKS

To eliminate the possibility of obtaining biased data due to the presence of NMOC in either the ultrapure air used for dilution of compressed gas standards or from the helium carrier gas, blank measurements were performed whenever support gas cylinders were changed and at other intervals. NMOC responses of less than 10 ppbC were always obtained for helium and the ultra-pure air.

MINIMUM DETECTABLE AMOUNT

Because the typical range of ambient NMOC is 100 to 5,000 ppbC, the lowest point of calibration was 70 ppbC. However, from the responses obtained at this concentration, it is estimated that the minimum concentration that could be reproducibly detected would lie between 10 and 50 ppbC, with a precision of ±15 percent.

PRECISION AND ACCURACY

The precision obtained in the evaluation of this method was found to be within ±5 percent for propane standard calibrations and single and multicomponent standard compressed gases. Usually, three consecutive analyses satisfied this criterion and, if not, two more analyses usually brought the standard deviation within these limits. The first analysis of a new sample was usually found to be erroneous, especially in the case of the aromatics tested, due to apparent adsorption onto the stainless steel sample lines.

Most of the NMOC values for ambient air samples (see Table 3) collected in stainless steel canisters fell within ±15 percent of the NMOC values obtained by manual gas chromatography, which probably indicates the actual accuracy that can be reached. The analyses that showed the highest percentage error using the GC analysis results as a reference were for the lower concentration samples where the large contamination peak was noted in the GC measurement. Overall, the NMOC technique averaged 45 ppbC higher than the GC results for the 12 analyses.

CALIBRATION

The dilution of propane standard (Scott B-237; 19.9 ppmV propane/balance in hydrocarbon-free air) and other hydrocarbon test gases (see Table 1) was done in a glass mixing manifold of about 450-cm^3 volume. Ultrapure air for dilution was prepared by catalytic cleanup of commercial breathing air (National Welders) using a palladium-on-alumina catalyst bed heated to 230° C and subsequent scrubbing by 5A molecular sieve and Purafil®. The efficiency of the cleanup system was checked periodically with propane.

Dilution air and standard gas flow rates were controlled either with very fine metering valves or electronic mass flow controllers, but in either case, the flow rates used for dilution calculations were obtained from direct soapfilm flowmeter measurements or from recent calibrations of mass flow controllers vs. a soapfilm flowmeter.

A periodic multipoint calibration (of at least 5 points) with the propane standard was performed over the range of 50 to 2,000 ppbC using instrument range X100 according to procedure. Triplicate injections were made for each concentration point, and then the average response (area/ppmC) for each concentration was calculated. The calibration point was accepted if the relative standard deviation for each set of triplicate injections was ≦ ±5 percent. The low concentration points (i.e., below 200 ppbC) deviated slightly from the linear curve and, therefore, extra calibration points were taken in the range of 50 to 200 ppbC. A typical calibration curve (ppbC vs. integrated peak response) is shown in Figure 12. The calibration curve was found as two straight-line segments: the first from zero to about 150 to 200 ppbC and the second from 150 to 200 ppbC up to and beyond the 2,000 ppbC calibration point.

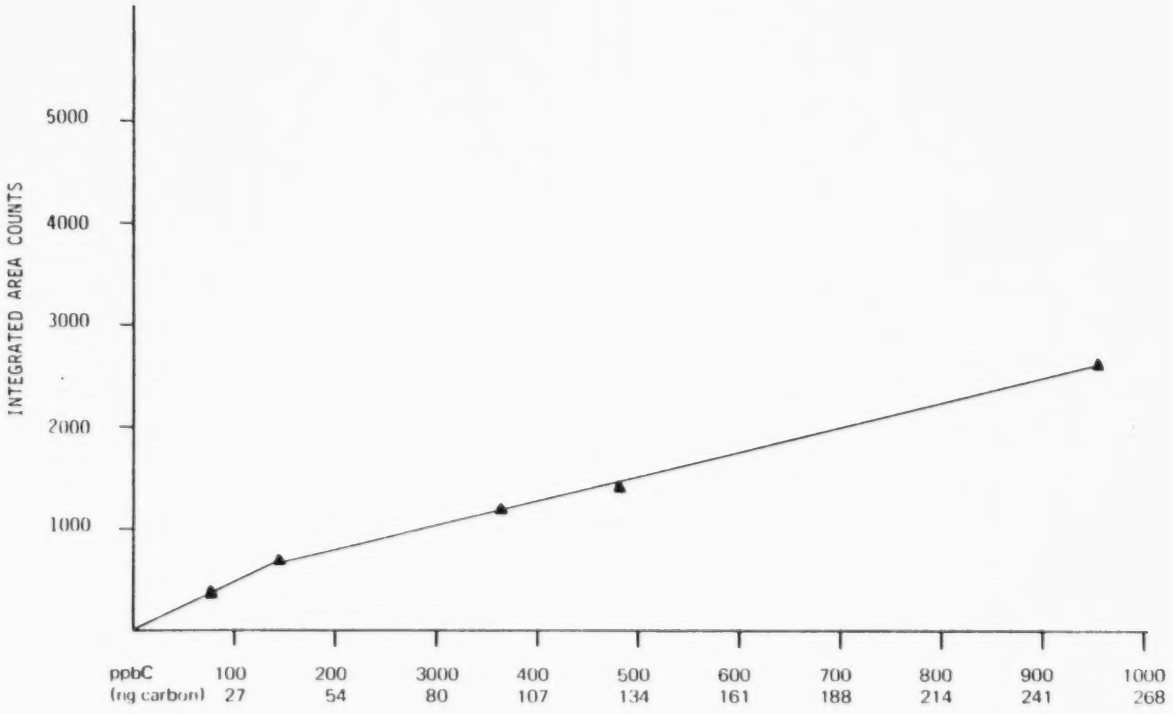

Figure 12. Typical propane calibration.

Prior to daily analysis of standards or samples, one or two propane calibration points were verified, and a complete multipoint calibration was performed if they deviated more than ±5 percent from previous calibration data or whenever the Beckman 400 had been shut down for repairs.

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APPENDIX A

METHOD DESCRIPTION AND PROCEDURE

INTRODUCTION

A variety of photochemical dispersion models have been developed to describe the quantitative relationships between ambient concentrations of precursor organic compounds and subsequent downwind concentrations of ozone.[1] An important application of such models is to determine the degree of control of such organic compounds that is necessary in a particular area to achieve compliance with applicable ambient air quality standards for ozone.[1,2] For this purpose, the models require input of nonmethane organic compounds (NMOC) concentration data.

The more elaborate theoretical models generally require detailed organic species data.[2] Such species data must be obtained by analysis of air samples using a sophisticated, multicomponent gas chromatographic (GC) analysis system.[2,3] Simpler empirical models such as the Empirical Kinetic Modeling Approach (EKMA) require only total NMOC concentration data, specifically the average total NMOC concentrations from 6 a.m. to 9 a.m. daily.[2]

For many EKMA applications, NMOC measurements are required at urban, center-city-type sites.[2] The moderately high NMOC concentrations typically found at such urban sites can be adequately measured by commercially available continuous (or semicontinuous) NMOC analyzers.[2,4] However, if transport of precursors into an area is to be considered, then NMOC measurements upwind of the area are necessary.[1] Upwind NMOC concentra-

tions are likely to be very low (less than a few tenths of 1 ppm) and, therefore, may not be accurately measured by conventional NMOC anlayzers.[2,4] NMOC GC species measurements can be used by summing the various components to obtain a total NMOC concentration.[2] But for EKMA, the species data are not needed, and the cost of species analysis is very high.

The method described herein can be used to obtain the requisite upwind NMOC measurements.[5,6] This method is a compromise between the continuous and GC methods mentioned above. It combines the cryogenic concentration technique used in the GC method for high sensitivity with the simple flame ionization detector (FID) for total NMOC measurements without the complex GC system necessary for species separation. And because of the use of helium carrier gas, the FID has less response variation to various organic compounds than a conventional NMOC analyzer with direct air injection.

This method can be used either for direct, in situ ambient measurements or for analysis of integrated samples from a sample bag or canister. Making direct measurements at the monitoring site avoids the potential sample loss or contamination problems inherent with the use of bags or canisters. However, the analyst must be present during the 6 to 9 a.m. period, and repeated measurements must be taken to obtain the 6 to 9 a.m. average NMOC concentration. A separate analytical system and analyst (or a conventional NMOC analyzer) is needed for each monitoring site.

The use of sample bags or canisters allows the collection of integrated air samples over the 6 to 9 a.m. period by automated samplers at unattended monitoring sites. One analytical system can then analyze the

samples from several monitoring sites. But degradation or contamination of the air samples by the bag or canister may be a significant problem.

One possible compromise is to locate the analytical system at the upwind site for direct measurements of the low upwind NMOC concentrations, with integrated bag or canister samples collected at the urban monitoring sites. Direct measurements are carried out during the 6 to 9 a.m. period after which the bag or canister samples from the urban site are brought to the upwind site for subsequent analysis. The higher concentrations at the urban sites will minimize the effect of losses or contamination of the bag or canister samples, while the low, upwind concentrations are measured directly. All measurements can be made with a single analytical system.

1. APPLICABILITY

This method is applicable to measurements of total gaseous nonmethane organic carbon (NMOC) concentrations in the atmosphere for use with atmospheric photochemical models such as EKMA.[1] Measurements may be obtained either in situ, or by subsequent analysis of integrated air samples collected over a fixed time period such as the 3-hour (6 to 9 a.m.) measurements specified for EKMA. Collection of integrated samples also allows for remote analysis of samples from multiple sites. The high sensitivity and low detection limit of the method make it suitable for upwind measurements, while the wide dynamic range allows analysis of urban air samples as well.

2. PRINCIPLE

An air sample is taken either directly from the ambient air at the monitoring site or from a sample bag or canister filled previously at the

site. A fixed-volume portion of the sample is drawn at a low flow rate through a tubular trap cooled to approximately -185° C. This temperature is such that most, if not all, organic compounds in the sample other than methane are trapped (either via condensation or adsorption) in the tube, while methane, nitrogen, oxygen, etc., pass on through. The system is dynamically calibrated so that the volume of sample passing through the trap does not have to be quantitatively measured, but must be precisely repeatable between the calibration and analytical phases.

After the fixed volume air sample has passed through the trap, a flow of helium is flushed through the trap and into a commercially available FID analyzer that is modified to operate with a helium carrier. When the residual methane and oxygen have been cleared from the trap and the FID baseline becomes steady, the temperature of the trap is raised to approximately 70° to 80° C. The organic compounds collected in the trap revolatilize and are carried into the FID, resulting in a response peak or peaks on a chart recorder connected to the FID analyzer output. The area of the peak is integrated, and the integrated value is translated to concentration units via a previously obtained calibration curve relating integrated reading with known concentrations of propane.

The cryogenic trap simultaneously concentrates the nonmethane organic compounds and separates and removes methane. Thus the technique is both direct reading for NMOC and more sensitive than conventional NMOC analyzers. Also, operation of the FID analyzer with a helium carrier results in less response variation to different organic compounds than is observed with conventional NMOC analyzers having direct air injection. Quantitative trapping has been shown for most compounds tested.[5]

3. PRECISION AND ACCURACY

Precision has been found to be within ±5 percent for standard gas calibrations and generally ±10 percent for ambient samples. Accuracy for ambient air samples collected in stainless steel canisters has been determined to be ±15 percent by comparison with manual GC analysis. Experimental results also show no significant effect from humidity over a wide range of concentrations.

4. APPARATUS

The following components and materials are required or recommended. Sources for the more specialized components are given in Appendix B. An overall schematic diagram of the analytical system is shown in Figure A-1, and a suggested system for collecting ambient samples in canisters or bags is shown in Figure A-2. A canister cleaning system is shown in Figure A-6.

4.1 Direct Sampling

4.1.1 Sample manifold or sample inlet line, to bring air sample into the analytical system.

4.1.2 Vacuum pump. Inexpensive vacuum pump or blower to draw air sample through sample manifold or inlet line with a low residence time.

4.2 Sample Collection in Pressurized Canisters

4.2.1 Sample canisters. Stainless steel pressure vessels of 4- to 6-L volume having electropolished interior and integral, leak-free shut-off valve (see Appendix). Each canister should have a unique identification number and a permanent log book.

4.2.2 Sample pump Metal Bellows model MB-151 or equivalent, capable of 2 atmospheres (30 psig) output pressure. Pump must be clean and uncontaminated by oil or organic compounds.

4.2.3 Auxiliary pump. Inexpensive vacuum pump to draw air sample through inlet line to sample pump with a low residence time.

4.2.4 Pressure gauge. 0-200 kPa (0-30 psig).

4.2.3 Shut-off valve.

4.2.6 Stainless steel capillary. Internal diameter 0.025 cm; length as required (see Section 6.2).

4.2.7 Vacuum pump. Capable of evacuating the sample canisters to an absolute pressure of 10^{-3} mm Hg.

4.2.8 Vacuum manifold. A stainless steel manifold with connections for several canisters to be simultaneously cleaned.

4.2.9 Bellows valve. A low leakage vacuum valve placed in-line between the vacuum pump and the vacuum manifold.

4.2.10 Vacuum gauge. Capable of measuring the vacuum of the vacuum manifold to an absolute pressure of 10^{-3} mm Hg.

4.2.11 Insulated heater box. Capable of heating stainless steel canisters to 150° C for cleanup.

4.2.12 Needle valve. Fine metering valve to adjust flow of sample from canister during analysis.

4.2.13 Cryogenic trap. Cooled with liquid nitrogen to prevent contamination from back diffusion of oil from the vacuum pump.

4.3 Sample Collection in Bags

4.3.1 Sampling bag. Tedlar, 8- to 12-L capacity, with shut-off valve.

4.3.2 Sample pump. Noncontaminating, to fill bags over required time period. System described for canisters may be used without the pressure gauge.

4.3.3 Vacuum pump. Inexpensive type to evacuate bags prior to use.

4.4 Analytical System

4.4.1 FID TOC analyzer. Beckman model 400 Hydrocarbon Analyzer, modified for helium carrier input as described in Section 6.4.8, or equivalent.

4.4.2 Six-port chromatographic valve. Valco model 9110, or equivalent.

4.4.3 Trap. Fabricated from a 120-cm length of 0.3175 cm (1/8 in.) o.d., 0.21 cm i.d. chromatographic grade stainless steel tubing to the dimensions shown in Figure A-3.

4.4.4 High pressure regulator. Standard, two-stage cylinder pressure regulator, with pressure gauges, for helium cylinder.

4.4.5 Low pressure regulator. Single stage with pressure gauge, to maintain constant helium carrier gas flow rate.

4.4.6 Needle valve. Fine metering valve to adjust sample flow rate through trap.

4.4.7 Cryogenic Dewars (2). Sized to contain submerged portion of trap, to hold liquid cryogen and hot water.

4.4.8 Absolute pressure gauge. 0 to 200 torr, Wallace-Tiernan model 61D-ID-0200, or equivalent.

4.4.9 Vacuum reservoir. Vacuum tank of about 2-L capacity.

4.4.10 Gas purifiers. Gas scrubbers containing Drierite or silica gel and 5A molecular sieve to remove moisture and organic impurities in the helium carrier gas, air, and hydrogen.

4.4.11 Shut-off valves (2). Leak free.

4.4.12 Vacuum pump. Capable of evacuating the vacuum reservoir to a pressure of 10 torr.

4.4.13 Chart recorder. Of suitable input voltage and chart speed to record graphic record of peaks from the FID analyzer.

4.4.14 Integrator. Or integrating chart recorder in lieu of 4.4.13, compatible with FID analyzer output and suitable to integrate peak areas. (See also Section 6.4.11.)

4.5 Other Materials

4.5.1 Various connecting tubing and plumbing fittings. All such items in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert material.

4.5.2 Various mechanical mounting fixtures as necessary.

5. SUPPLIES

5.1 Helium. Cylinder of zero-grade helium containing less than 0.5 ppmC hydrocarbons.

5.2 Combustion air. Cylinder of zero-grade air containing less than 0.5 ppm hydrocarbons, or equivalent air source.

5.3 Hydrogen. Cylinder of pure hydrogen containing less than 0.5 ppmC hydrocarbons, or equivalent hydrogen source.

5.4 Propane calibration standard. Cylinder containing 5 to 100 ppm propane in air. Cylinder assay should be traceable to a National

Bureau of Standards (NBS) propane in air Standard Reference Material (SRM) or a commercially available Certified Reference Material (CRM).

5.5 Zero air. Air containing less than 0.01 ppmC hydrocarbons. May be obtained from a cylinder of zero-grade compressed air scrubbed with Drierite or silica gel and 5A molecular sieve or activated charcoal, or by catalytic cleanup of ambient air. The efficiency of the cleanup system should be checked periodically with propane.

5.6 Liquid oxygen or liquid argon.

5.7 Hot water, 70° to 80° C.

6. SYSTEM DESCRIPTION

6.1 Direct Sampling

A portion of the air flowing in the inlet manifold or inlet line is removed with a TEE connection and delivered directly to port five of the six-port valve. This connecting line should be kept as short as possible to minimize its dead volume. The NMOC measurement will represent the average NMOC concentration in the air sample during the trapping phase (about 10-20 minutes). Direct sampling avoids potential sample degradation or contamination from sample collection containers.

6.2 Sample Collection in Pressurized Canisters

Collection of ambient air samples in pressurized canisters provides a number of advantages, including (1) integration of ambient samples over a time period, e.g., 3 hours; (2) remote sampling and central analysis; (3) storage and shipping of samples; (4) unattended sample collection; (5) analysis of samples from multiple sites; and (6) collection of replicate samples for statistical analysis. However, great care must be

exercised in selecting, cleaning, and handling the sample canisters and sampling apparatus to avoid losses or contamination of the samples.

Figure A-2 shows a schematic of a recommended sample collection system. The small auxiliary pump purges the inlet manifold or lines with a flow of several liters/minute to minimize the sample residence time. The larger Metal Bellows pump (MB-151) takes a small portion of this sample stream and pressurizes it to fill the canisters. Both pumps should be shockmounted to a plywood base, which should also have rubber feet, to minimize vibration.

The capillary connecting the outlet of the Metal Bellows pump to the canisters is used to limit the flow into the canisters and must be cut to a length that provides the desired flow rate. This flow rate is chosen so that the canisters are pressurized to at least 1 atmosphere above ambient pressure (2 atmospheres absolute pressure) over the desired sample period. The flow rate can be calculated by

$$F = \frac{P\ V\ N}{T \times 60} \qquad (1)$$

where

F = Flow rate, cm^3/min;

P = Final canister pressure, atmospheres absolute;

V = Volume of the canister, cm^3;

N = Number of canisters;

T = Sample period, hours; and

60 = 60 min/hour.

For example, if two 4-L canisters are to be filled to 2 atmospheres absolute pressure (15 psig) in 3 hours,

$$F = \frac{2 \times 4000 \times 2}{3 \times 60} = 89 \text{ cm}^3/\text{min}.$$

The canisters are originally evacuated, and once they are filled to above atmospheric pressure (about half the sample period), then pressure can be monitored with the pressure gauge. The connecting lines between the capillary and the canisters should be as short as possible to minimize their volume. Be sure the pump outlet pressure is at least 1 atmosphere higher than the final canister pressure so that the flow rate remains constant over the entire sampling period.

At least two canisters should be filled simultaneously in case one is contaminated or lost by leakage. Three or more canisters filled simultaneously would offer even greater protection, and replicate samples provide useful quality control information.

Prior to field use, each sampling system should be tested for pump contamination (see Section 7.2), leaks, and proper flow rate. The plumbing on the outlet side of the Metal Bellows pump can be checked for leaks by shutting off the canister valves, pressurizing the system, and checking fittings, etc., with a nonhydrocarbon-based leak detector fluid. The MB-151 pump should also be leak checked by plugging its outlet and ensuring that there is no flow into its inlet side, using a soap film flowmeter. The canisters must be cleaned and checked for contamination before use (see Section 7.1).

During analysis, a pressurized canister is connected to port five of the six-port valve via a needle valve (V4) and vent as shown in Figure A-1. The needle valve reduces the canister pressure and adjusts the canister flow rate to a value slightly higher than the trap flow rate set by valve

V3. The excess flow exhausts through the vent, which assures that the sample air flowing through the trap is at atmospheric pressure. The vent is submerged in water so that the escaping bubbles provide a visual indication of vent flow and assist in adjusting valve V4.

6.3 Sample Collection in Bags

Sample bags are simpler, more readily available, and less expensive than canisters. But bags cannot be cleaned with heat and vacuum as canisters can, and contamination from bag outgassing or permeation through the bag may be a significant problem. Bag samples must be analyzed within 3 hours and must be protected from heat and sunlight. Containing the sample bags in cardboard boxes is recommended.[6]

6.4 Analytical System

6.4.1 Sample volume metering system. The vacuum reservoir and pressure gauge (see Figure A-1) are used to meter precisely repeatable volumes of sample air through the cryogenic trap. With valve V2 closed and valve V1 open, the reservoir is first evacuated with the vacuum pump. Then V1 is closed and V2 is opened to allow a fixed volume of air to enter the reservoir via the trap and six-port valve. The volume of air sampled is determined by the pressure rise measured by the pressure gauge. This volume can be calculated by

$$V_s = \frac{\Delta P \; V_r}{P_s} \qquad (2)$$

where

V_s = Volume of air sampled, standard cm^3;

ΔP = Pressure difference measured by gauge, torr;

V_r = Volume of vacuum reservoir, standard cm^3; and

P_s = Ambient pressure, torr.

For example, with a vacuum reservoir of 1700 cm^3 and a pressure change of 180 torr (20 to 200), the volume sampled would be 403 cm^3. The actual reservoir volume is noncritical, since it will be constant throughout calibration and sample analysis, but changing the volume of the sample will change the sensitivity of the method. Sample volumes of 200 cm^3 to 500 cm^3 appear to be appropriate for typical ambient NMOC concentrations. If the response peak obtained for a 500-cm^3 sample turns out to be outside the calibration range or off scale, a second analysis of a 250-cm^3 sample can be carried out.

6.4.2 Trap. The trap should be carefully constructed from a single piece of tubing in the shape shown in Figure A-3. The trap is left hollow, as packing is unnecessary and tends to cause flow changes as the trap is warmed during analysis. The coil must fit conveniently into the Dewar flasks (Section 4.4.7), and the arms must be of an appropriate length to allow the coil to be completely submerged below the level of liquid cryogen in the Dewar. The trap should connect directly to the six-port valve to minimize line length between the trap and the FID analyzer. Also, it must be mounted to allow the Dewars to be conveniently slipped on and off the trap.

6.4.3 Liquid cryogen. Either liquid oxygen (bp -183.0° C) or liquid argon (bp -185.7° C) may be used for the cryogen; experiments have shown no difference in trapping efficiency between the two

cryogenic liquids.[5] However, appropriate safety precautions must be taken if liquid oxygen is used. Liquid nitrogen (bp -195° C) should not be used as the cryogen as it causes condensation of oxygen and methane in the trap. The level of the liquid seems to be important, so it should be initially constant at a point that completely covers the trap coils.

6.4.4 Heat source. To facilitate integration of the NMOC response peak, a hot bath is used to volatilize the concentrated NMOC so it is seen by the FID as one or only a few sharp and easily integrated peaks. Without using hot water, components of the sample "fractionally distill" off the trap as it warms up to room temperature and a series of small, hard-to-integrate peaks result. The water should be heated to above 75° C but not to boiling (100° C). A simple heating source is an electrical immersion heater, which readily heats about 1 L of water to 75° to 85° C.

6.4.5 Carrier gas. Helium is used to purge residual air and methane from the trap at the conclusion of the sampling phase, and to carry the revolatilized NMOC from the trap into the FID. The helium flow of 76 cm^3/min is determined by the sample capillary in the FID analyzer and the pressure setting of the single-stage regulator. This single-stage regulator may not be necessary, but it is recommended to regulate helium pressure better than the two-stage cylinder regulator. When used, the secondary stage of the two-stage regulator must be set at a pressure higher than the pressure setting of the single-stage regulator.

6.4.6 Gas purifiers. Carrier helium, burner air, and burner hydrogen should all be passed through Drierite/Molecular Sieve 5A gas purifiers to remove water, oil, and organics from these support gases. If commercial "zero-air" is used for dilution purposes, it too should be passed through a scrubber, and if possible, an MSA Model 458060 (or equivalent) catalytic oxidizer to remove contaminant hydrocarbons that are frequently found in commercial zero-air. The efficiency of the catalytic oxidizer system should be checked periodically with propane.

6.4.7 Construction. The configuration of analytical components shown in Figure 4 has all the hardware (except the FID analyzer) mounted on an aluminum panel that fits into an aluminum suitcase with outside dimensions 45.7 × 44 × 30.5 cm. By using aluminum angle around three sides of the panel, the analytical assembly can be attached directly to the angle and easily removed from the case.

All tubing used for the system should be 0.3175 cm (1/8 in) stainless steel connected with stainless steel fittings. Connections for vacuum and helium carrier gas are made through bulkhead fittings on the panel. Other connections are made directly to the six-port valve. The stainless steel line to the analyzer from the six-port valve should be kept as short as possible to avoid losses due to cooling, adsorption, and spreading of the sample peak. The trap is shown connected directly to the valve, and the entire valve assembly is offset 5 cm from the panel to provide clearance for the Dewars.

After assembly, the system should be carefully checked for leaks. The leak check may be accomplished by plugging the sample inlet (port 5 on the valve); opening valves V1, V2, and V3; turning the 6-port valve to the sample position; and evacuating the system. Then close valve V1 and observe the pressure reading on the absolute pressure gauge. If the pressure reading remains steady for several hours, the system can be considered free of leaks. Pressurized portions of the system (hydrogen, helium, and air lines) may be checked with liquid leak detector.

6.4.8 FID analyzer. The Beckman 400 Total Hydrocarbon Analyzer must be modified as shown in Figure A-5. The physical modification consists of disconnecting the original sample bypass line leading to the back-pressure regulator. The point at which this line was connected to a TEE fitting near the input port is capped off. Thus the entire sample input is directed through the sample capillary to the FID. The normal burner air and hydrogen flow rates are also changed to 650 cm^3/min for burner air and 45 cm^3/min for hydrogen. The use of these flow rates and the helium carrier instead of air carrier results in more uniform FID response to various hydrocarbon compounds.

6.4.9 Linearity. Response has been shown to be linear from 150 ppbC to 5000 ppbC with slightly nonlinear response below 150 ppbC.[5]

6.4.10 Range. The Beckman analyzer provides both a front panel "range" (attenuator) control and an internal full-scale output voltage selector. An appropriate combination should be chosen so that an adequate output level for accurate integration is

obtained down to the detection limit, yet the electrometer of the analyzer should not be driven into saturation at the upper end of the calibration. Saturation of the electrometer is indicated by a front panel meter reading of over 100 percent. Additional adjustment of range and sensitivity can be provided by the sample volume used, as discussed in Section 6.4.1.

6.4.11 Integrator. The integrator's input voltage range must match the output signal voltage range of the FID analyzer so that sufficient resolution is available at low concentrations without overranging on high concentrations. If both an integrator and a separate chart recorder are used, care must be exercised to be sure they don't interfere with each other electrically. Range selector controls on both the integrator and the FID analyzer may not provide accurate range ratios, so individual calibration curves should be prepared for each range to be used.

Setting the zero-baseline of the integrator is very important to the accuracy of the method. Consult the integrator instruction manual for proper setting of the baseline. In particular, a negative FID response may occur if the trap is heated too rapidly during analysis. Some automated integrators may thus select an incorrect zero baseline. It may be necessary to use an integrator whose zero baseline can be set manually. Also, since some slight baseline shift may occur when humid air samples are analyzed, one of the newer, more sophisticated

integrators that can automatically compensate for a baseline shift is recommended.

7. PROCEDURE

7.1 Recommended Procedure for Canister Cleaning

7.1.1 Connect canisters to the vacuum manifold in the heated box as shown in Figure A-6. Close the lid and heat to 150° C.

7.1.2 Open the canister shut-off valves and evacuate to 0.5 mm Hg, using a liquid-nitrogen-cooled trap on the vacuum line to eliminate back-diffusion of hydrocarbons and oil from the vacuum pump.

7.1.3 Close bellows valve V5 and shut-off valve V7. Open valve V6 to pressurize canisters to 40 to 60 psig (300 to 400 kPa).

7.1.4 Close valve V6 and allow the canisters to remain pressurized for 15 to 20 minutes.

7.1.5 Open valve V5 and evacuate the canisters to 0.5 mm Hg. Open valve V7 only after the manifold pressure is below ambient pressure to monitor the vacuum.

7.1.6 Allow the canisters to remain evacuated for 10 to 15 minutes. Then close valves V5 and V7.

7.1.7 Repeat steps 7.1.3 to 7.1.6 two times.

7.1.8 Fill canisters with zero air and analyze them for contamination using the FID analyzer system as a blank check of the cleanup system and procedures.

7.1.9 Reevacuate the canister after the analysis.

7.1.10 Attach a paper tag to each canister for field notes and take the container to the site.

7.2 Procedure for Collection of Samples in Pressurized Canisters

7.2.1 Leak-test all canisters by pressurization to 60 psig (400 kPa) with zero air and immersion in water.

7.2.2 Clean the canisters according to the procedure in Section 7.1. Any canisters that cannot be cleaned by repeated cleaning should not be used.

7.2.3 Check the pump for contamination by filling two evacuated, cleaned canisters with zero air and analyzing them.

7.2.4 Assemble a sample collection system such as the one shown in Figure A-2. All canisters used should be cleaned and checked for contamination according to Section 7.1.

7.2.5 Turn on pumps and allow them to warm up for 15 minutes. After warming up, check the flow rates (see Section 6.2) with a soap film flowmeter, then loosely attach the fittings to the canisters for at least 1 minute. Leave the canister valves and the gauge shut-off valve closed.

7.2.6 Without turning off the pumps, tighten the fittings, then open the canister shut-off valves.

7.2.7 The canisters will fill slowly over the selected period at the predetermined flow rate. At the end of the sample period, measure the pressure with the pressure gauge connected at the union cross to ensure that the canisters have been pressurized to 2 atmospheres.

7.2.8 Close canister valves and tighten. Remove them from the pump setup and recheck the sample flow rate to see if it has changed from the initial flow rate. Then turn off the pumps.

7.2.9 The identification tags on the sample canisters should be filled out as necessary. Bring the canisters to the analytical system for analysis.

7.2.10 Complete records of the sampling should be entered in the canister log book. The sampling operator should be alerted to take note of any activities in the area that may affect the sample contents.

7.3 Procedure for Cleaning Sample Bags

7.3.1 Check bag for absence of leaks.

7.3.2 Evacuate bag and fill with zero air three times.

7.3.3 Let bag stand for 1 hour filled with zero air.

7.3.4 Analyze the zero air from the bag to see if contamination is insignificant.

7.3.5 Evacuate the bag and take it to the sampling site.

7.4 Procedure for Collection of Sample in Bags

7.4.1 Assemble a sample collection system such as the one shown in Figure A-2. Use only bags that have been cleaned and checked according to Section 7.3.

7.4.2 Start pumps and allow them to warm up for 15 minutes. Then check flow rate for proper value to fill bag over the required time period (see Section 6.2).

7.4.3 Fill bags; keep them away from heat and sunlight during sampling and transporting.

7.4.4 Analyze bag samples within 3 hours.

7.5 Analysis Procedure

7.5.1 Assemble the analysis system as shown in Figures A-1 and A-4 and as discussed in Section 6. Allow the FID analyzer to warm up and stabilize for several hours before analysis. Observe the operating procedures and safety precautions described in the FID analyzer's instruction manual.

7.5.2 Check and adjust helium pressure to provide a flow rate of 76 cm^3/min.

7.5.3 Close valve V2 and open valve V1 to evacuate the vacuum reservoir.

7.5.4 With the trap at room temperature, place the six-port valve in the inject position.

7.5.5 Open valve V2 and adjust valve V3 for a sample flow of 45 to 60 cm^3/min.

7.5.6 Connect sample canister, bag, or direct sample inlet to port five of the six-port valve as shown in Figure A-1. For a canister, open the canister valve and adjust valve V4 to obtain a slight vent flow as indicated by constant bubbles. (CAUTION: Do not allow water to be drawn into the six-port valve.) Then close valve V2. Also, significantly better recovery of aromatics from a canister can be obtained by heating the canister to about 80° C with heating tape or a heated enclosure.

7.5.7 Open valve V1 (if not already open) to evacuate the vacuum reservoir. With the six-port valve in the inject position and valve V1 open, open valve V2 for a few minutes to flush and condition the inlet lines. Close valve V2.

7.5.8 Submerge the trap in the cryogen and check and maintain the initial cryogen level constant so that it completely covers the coils of the trap (i.e., to the same level used during calibration). Allow a few minutes for the trap to cool completely.

7.5.9 With the six-port valve still in the inject position, close valve V1 and open valve V2.

7.5.10 Observe the increasing pressure on the pressure gauge; when it reaches an arbitrary point such as 20 mm Hg, quickly switch the six-port valve to the sample position.

7.5.11 Observe the increasing pressure on the pressure gauge; when it reaches a second arbitrary point such as 200 mm Hg, quickly switch the valve to the inject position, keeping the cryogenic bath on the trap. Close valve V2 to conserve the remaining sample in the canister or bag.

7.5.12 Start the chart recorder, and wait until the response baseline has stabilized (about 3 to 5 minutes). Do not wait longer than 7 minutes.

7.5.13 Start the integrator. Remove the liquid cryogenic bath, wait 20 seconds, and then smoothly but not too quickly immerse the trap in hot water (approximately 80° C). Use the same level of hot water for both calibration and sample analyses. Placing the hot water on too quickly may cause an initial negative-going response which could hamper accurate integration.

7.5.14 Observe the response peak. Determine the total NMOC integrated peak area and use the calibration curve to convert the reading into concentration units (ppbC). Note that the NMOC

peak shape may not be reproducible due to differences in placing the hot water on the trap, but the total NMOC peak area should be reproducible.

CAUTION:

It has been determined that organic contamination in the trap and/or sample lines can be released by water vapor from especially humid samples, and that this contamination can result in false, high values. This contamination is indicated by an unusually broad NMOC peak or long tailing (more than one minute). The contamination should be removed by heating the NMOC trap electrically or with a hot air blower while the six-port valve is in the injection position and helium is flowing. The absence of contamination should be tested by analysis of humidified clean air or a humidified standard. If neither of these shows unusually broad peaks, long tailing, or yields higher than expected peak areas, one can assume the system is acceptable for sample analysis.

To obtain better quality data, the following tests should be performed daily before start of the first analysis:

1. Heat the NMOC trap and stainless steel lines daily with a hot air blower or electrically with helium flowing.
2. Perform analyses of both dry and humidified clean air samples and compare the responses. No significant difference in hydrocarbon response between the two

samples indicates that the analytical system is ready for use.

7.5.15 Blot the trap dry. If analyzing a bag or canister, repeat the analysis two or three times and report the average NMOC concentration.

8. CALIBRATION

8.1 Calibration Frequency

Initially a complete dynamic calibration of five or more points should be carried out on each range to define the calibration curve. Subsequently, the calibration should be verified with two- or three-point calibration checks (including zero) two or three times per week or each time the analytical system is restarted after being shut down.

8.2 Calibration Standards

Propane calibration standards may be obtained directly from low-concentration cylinder standards or by dilution of high-concentration cylinder standards with zero air. Dilution flow rates must be measured accurately, and the combined gas stream must be mixed thoroughly. Calibration standards may be sampled directly from the flowing stream, or sample bags or canisters may be filled and analyzed. Remember that a propane concentration in ppmC is three times the volumetric concentration in ppm.

8.3 Calibration Procedure

8.3.1 Select one or more combinations of FID analyzer attenuator setting, output voltage setting, integrator resolution (if applicable), and sample volume to provide the desired range or ranges (e.g., 0-500 ppbC or 0-5000 ppbC). Each such range

should be calibrated individually and have a separate calibration curve.

8.3.2 Analyze each calibration standard three times according to the procedure in Section 7.5. Be sure that flow rates, initial liquid level in the Dewars, timing, and other variables are the same as will be used during analysis of ambient samples.

8.3.3 Average the three results for each concentration standard and plot the calibration curve(s) as integrator peak area reading versus concentration in ppbC. Linearity should be expected, at least above 150 ppbC. Points that appear to deviate abnormally should be repeated. Relative standard deviation for the three analyses should be less than 5 percent. If nonlinearity is observed at low concentrations, additional points in that region may be needed to adequately define the calibration curve.

9. METHOD MODIFICATIONS

9.1 Sample Metering System

Although the vacuum reservoir and absolute pressure gauge technique for metering the sample volume is efficient and convenient, other techniques should work also. For example, a constant sample flow could be established with a vacuum pump and a critical orifice, with the six-port valve being switched to the sample position for a measured time period. Or a gas volume meter such as a wet test meter could be used to measure the total volume of sample air. However, these alternate techniques have not been tested or evaluated.

9.2 TOC Analyzer

FID analyzers other than the Beckman model 400 specified may also be adaptable to the method. The specific flow rates and necessary modifications for the helium carrier for any alternate FID would have to be worked out by the user.

9.3 Range

It may be possible to increase the sensitivity of the method by increasing the sample volume. However, other limitations are likely to arise; hence any attempts to increase the sensitivity should be tested carefully.

9.4 Alternate Carrier Gas

It may be possible to substitute nitrogen for the helium carrier, but no tests using a nitrogen carrier have been carried out.

9.5 Nonlinear Calibration

Although FID response is usually linear, tests during method development produced a nonlinear calibration below 150 ppbC.[5] No explanation for this is apparent. It may be possible to adjust the sample volume, FID attenuation, or integrator resolution to reduce this nonlinearity.

9.6 Trap Heating

Other techniques may be used for heating the trap during the analysis phase. For example, with a suitable temperature control, the trap could be heated electrically by passing electrical current directly through the trap tubing, heating the trap using its internal resistance.

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4. Sexton, F. W., F. F. McElroy, R. M. Michie, Jr., and V. L. Thompson. A Comparative Evaluation of Seven Automatic Ambient Non-Methane Organic Compound Analyzers. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, draft document, 1981.

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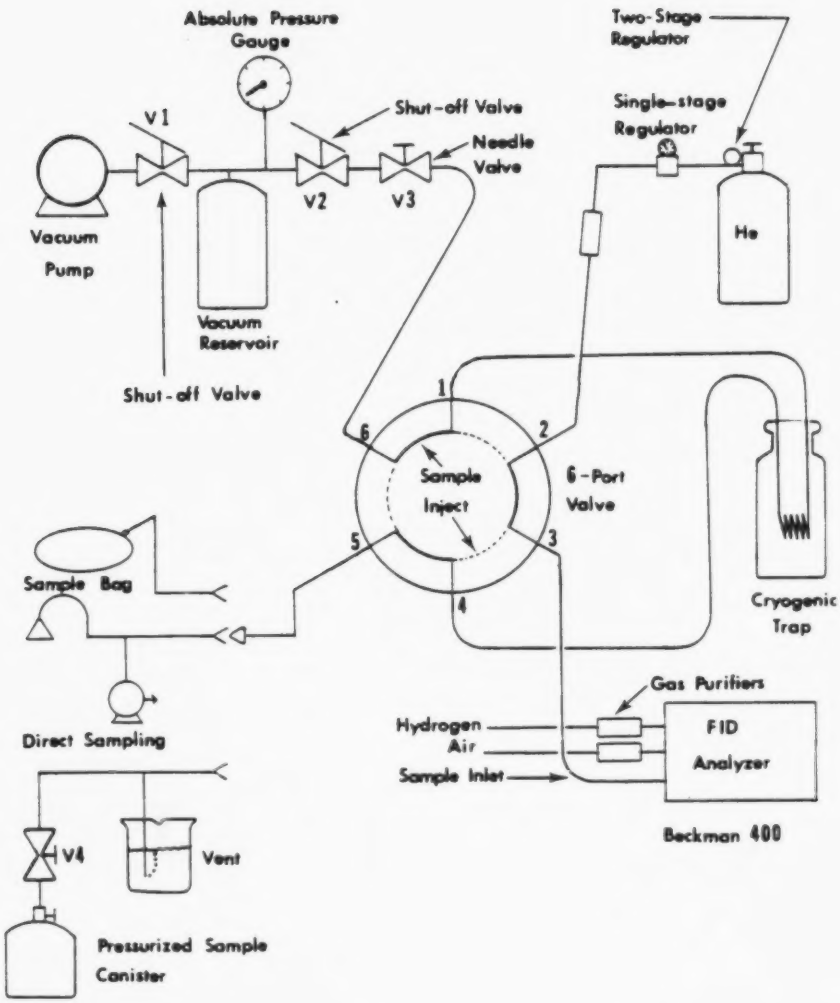

Figure A-1. Schematic of analysis system showing three sampling models.

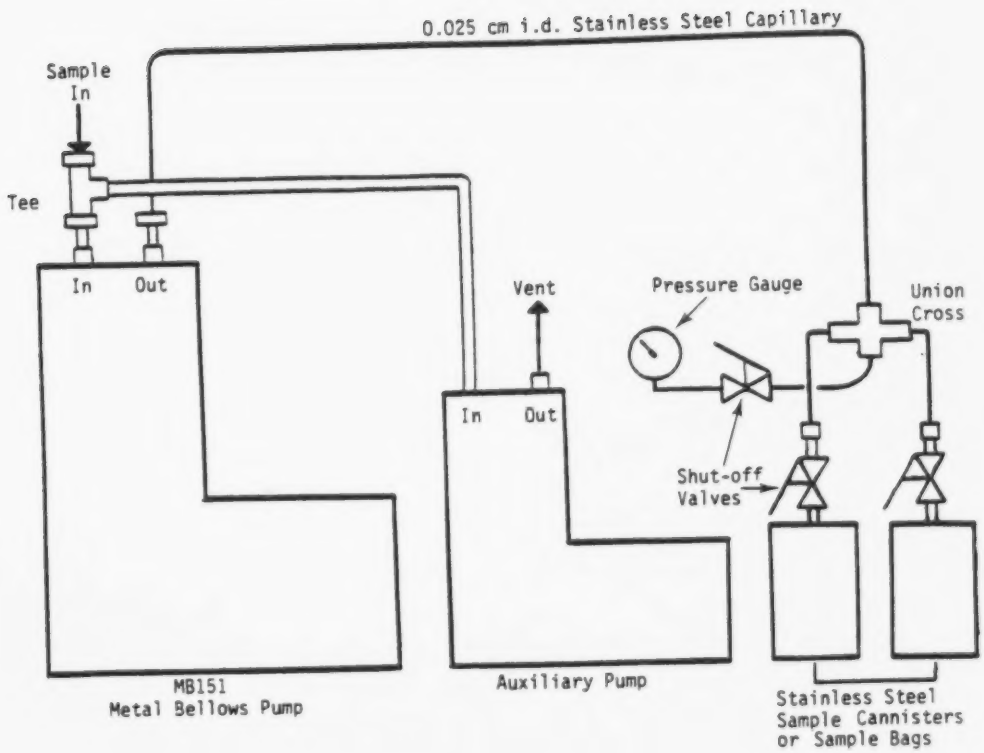

Figure A-2. Sample system for collection of integrated field samples.

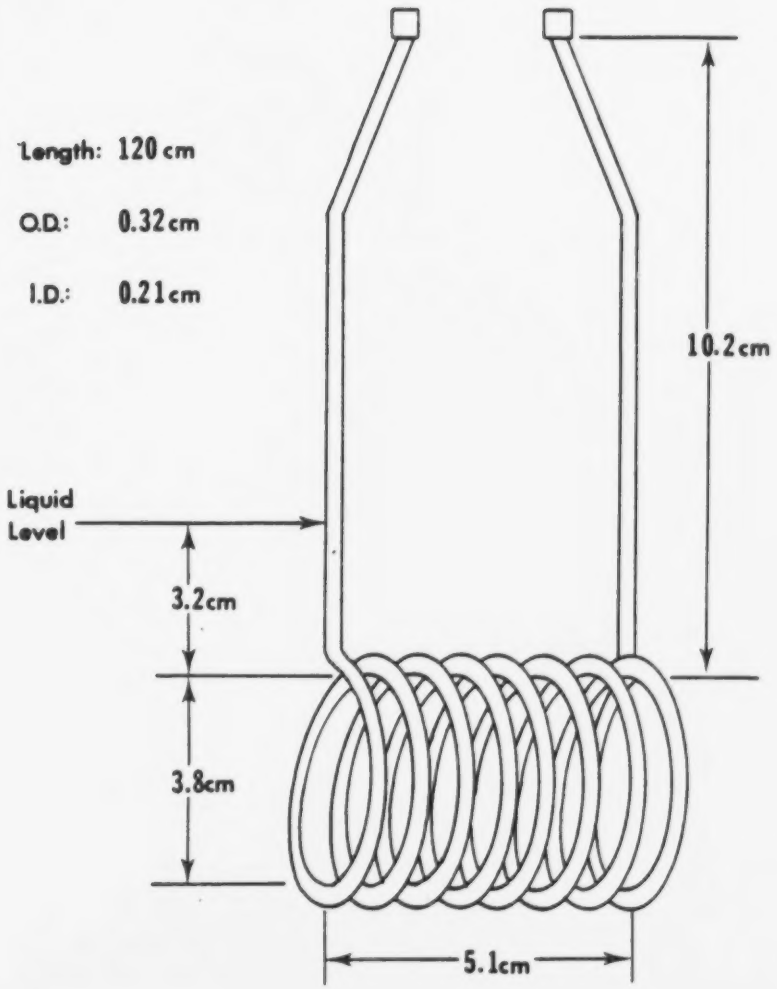

Figure A-3. Sample trap dimensions.

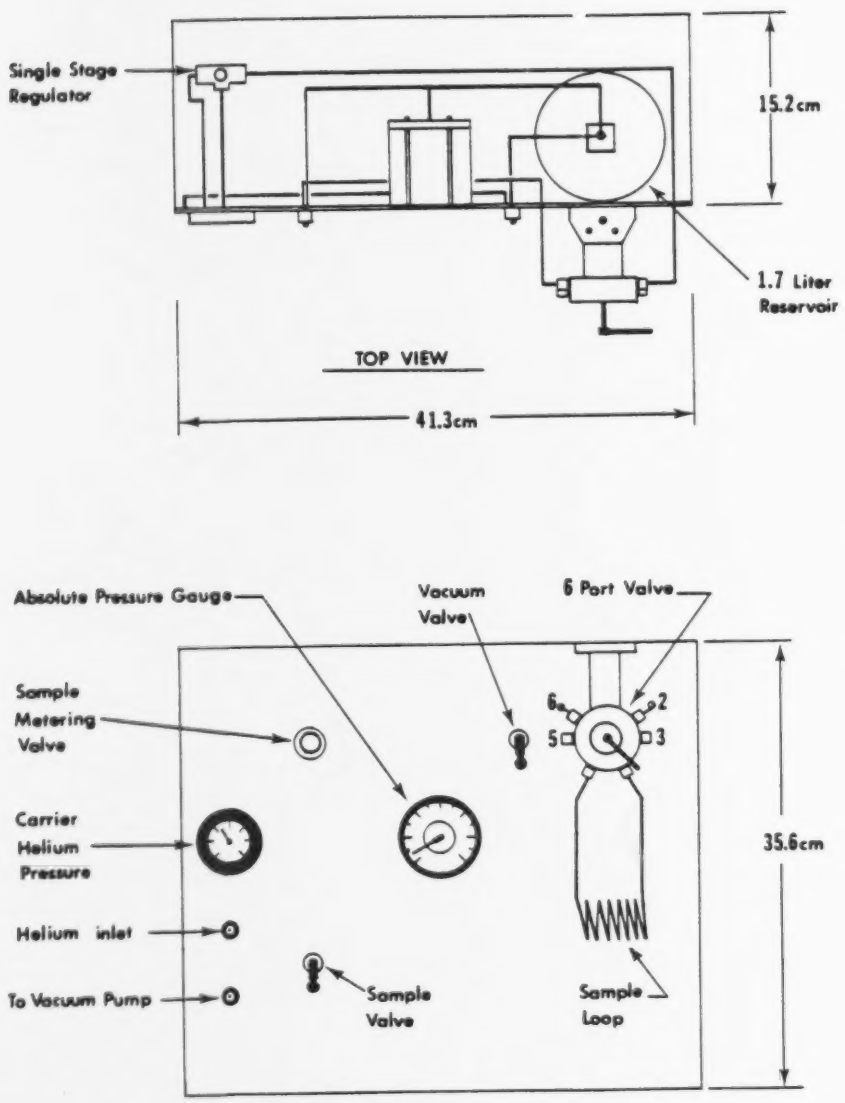

Figure A-4. A modular design for the analysis system.

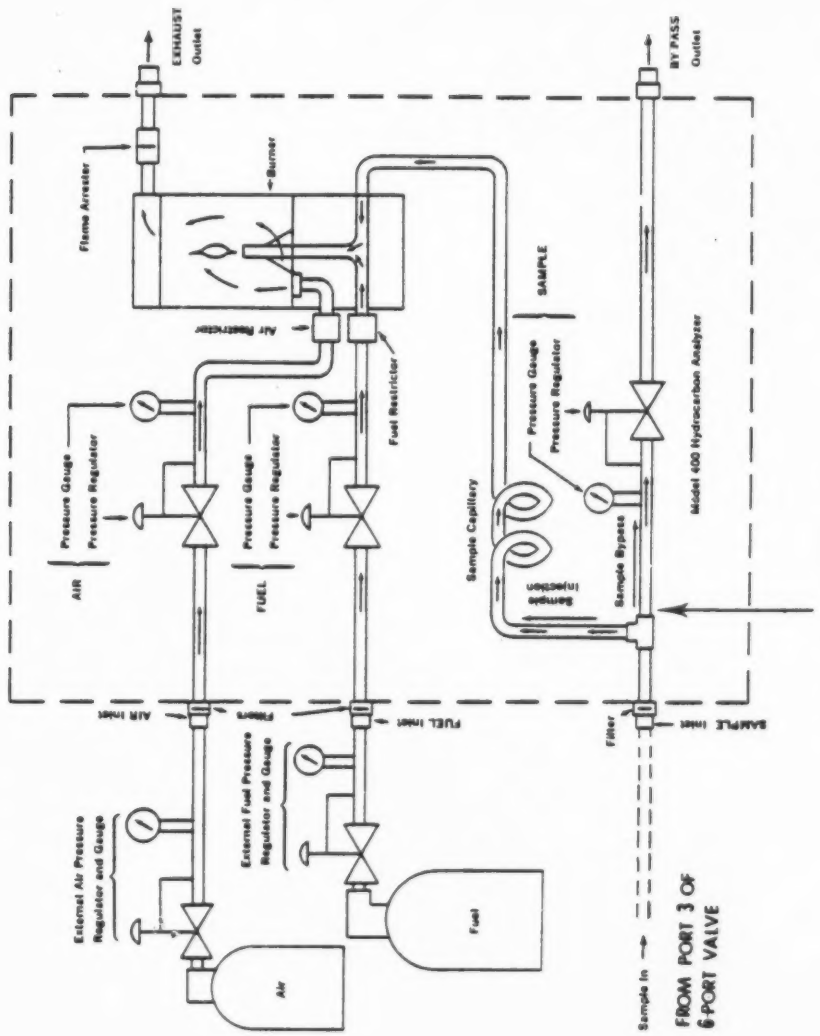

Figure A-5. Schematic of Beckman 400 hydrocarbon analyzer showing modification.

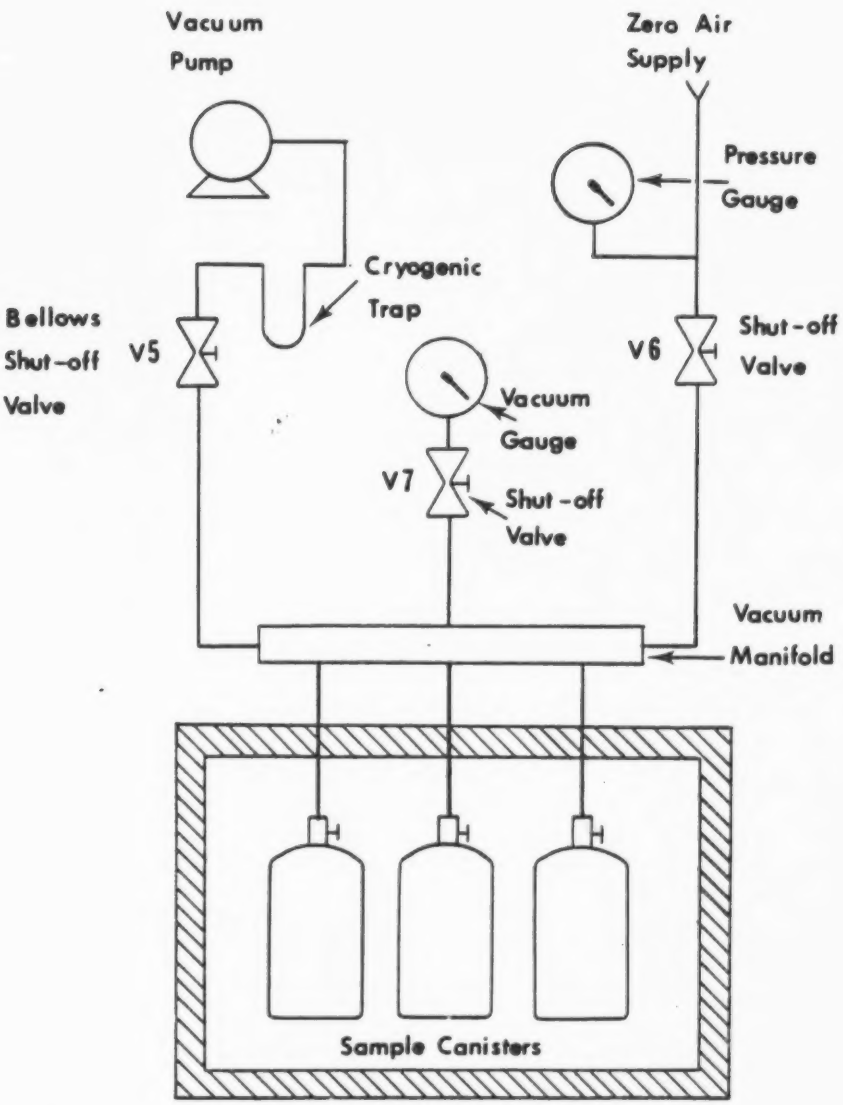

Figure A-6. Canister cleaning system.

APPENDIX B

SOURCES FOR SPECIALIZED COMPONENTS

MATERIAL	MODEL/DIMENSIONS	SUPPLIER
1. Sample Canister	4-6 Liter	D&S Instruments, Ltd. N. 1218C Grand Ave. Pullman, WA 99163 (509) 332-3684
2. Absolute Pressure Gauge	Model 61D-ID-0200, (0-200 mm Hg), 2-1/2 in. Face	Wallace & Tiernan Div. of Pennwalt Corp. 25 Main Street Belleville, NJ 07109
3. Six-Port Valve	Valco 9110	Alltech Associates 606A Union Street Kenneth Square, PA 19348
4. Gas Purifiers	Cat #8125	Alltech Associates
5. Chromatographic Grade Stainless Steel Tubing	Cat #30101 (1/8 in. × 0.085 in.)	Alltech Associates
6. Integrating Chart Recorder	Linear Model 252A	Cole-Parmer 7425 North Oak Avenue Chicago, IL 60648
7. Tedlar sampling bags	Catalog No. 1409	Horizon Ecology Company 7435 N. Oak Park Avenue Chicago, IL 60648
8. FID TOC Analyzer	Beckman Model 400	Beckman Instruments, Inc. Process Instruments Div. 2500 Harbor Boulevard Fullerton, CA 92634
9. Aluminum suitcase		Zero Corporation 777 Front Street Burbank, CA 91503
10. Metal Bellows pump	Model MB-151	Metal Bellows Corporation 1075 Providence Highway Sharon, MA 02067
11. Vacuum gauge	$0\text{-}10^{-3}$ mm Hg	Consolidated Vacuum Corporation
12. Cryogenic Dewar	10-196-10B (30 cm × 26 cm)	Fisher Scientific Company